DISSOLVED ORGANIC MATTER DISCHARGE IN THE SIX LARGEST ARCTIC RIVERS: CHEMICAL COMPOSITION AND SEASONAL VARIABILITY

A Thesis

by

AMANDA J. RINEHART

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2007

Major Subject: Oceanography

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Approved by:

Chair of Committee,	Rainer Amon
Committee Members,	Bruce Herbert
	Dan Thornton
Head of Department,	Robert Stickney

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ABSTRACT

Dissolved Organic Matter Discharge in the Six Largest Arctic Rivers: Chemical Composition and Seasonal Variability. (August 2007)

Amanda J. Rinehart, B.S., Texas A&M University

Chair of Advisory Committee: Dr. Rainer Amon

The vulnerability of the Arctic to climate change has been realized due to disproportionately large increases in surface air temperatures which are not uniformly distributed over the seasonal cycle. Effects of this temperature shift are widespread in the Arctic but likely include changes to the hydrological cycle and permafrost thaw, which have implications for the mobilization of organic carbon into rivers. The focus of this research was to describe the seasonal variability of the chemical composition of dissolved organic matter (DOM) in the six largest Arctic rivers (Yukon, Mackenzie, Ob, Yenisei, Lena and Kolyma) using optical properties (UV-Vis Absorbance and Fluorescence) and lignin phenol analysis. We also investigated differences between rivers and how watershed characteristics influence DOM composition.

Dissolved organic carbon (DOC) concentrations followed the hydrograph with highest concentrations measured during peak river flow. The chemical composition of peak-flow DOM indicates a dominance of freshly leached material with elevated aromaticity, larger molecular weight, and elevated lignin yields relative to base-flow DOM. During peak flow, soils in the watershed are still frozen and snowmelt water follows a lateral flow path to the river channels. As the soils thaw, surface water penetrates deeper into the soil horizons leading to lower DOC concentrations and likely altered composition of DOM due to sorption and microbial degradation processes. The six rivers studied here shared a similar seasonal pattern and chemical composition. There were, however, large differences between rivers in terms of total carbon discharge reflecting the differences in watershed characteristics such as climate, catchment size,

river discharge, soil types, and permafrost distribution. The large rivers (Lena, Yenisei), with a greater proportion of permafrost, exported the greatest amount of carbon. The Kolyma and Mackenzie exported the smallest amount of carbon annually, however, the discharge weighted mean DOC concentration was almost 2-fold higher in the Kolyma, again, indicating the importance of continuous permafrost. The quality and quantity of DOM mobilized into Arctic rivers appears to depend on the relative importance of surface run-off and extent of soil percolation. The relative importance of these is ultimately determined by watershed characteristics.

DEDICATION

This work is dedicated to my husband, Judson, who has been more supportive, loving, and understanding than I could have ever dreamed. I would also like to dedicate this to Forrest and Hayden who I hope will always find the inspiration to follow their curiosities and dreams. Also, to my parents who have been amazing throughout this whole process. Finally, to my Grandma who was my very first scientific mentor.

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

Page

ABSTRACT iii

DEDICATION v

ACKNOWLEDGEMENTS vi

TABLE OF CONTENTS vii

LIST OF FIGURES ix

LIST OF TABLES xiv

CHAPTER

I INTRODUCTION 1

II STUDY SITE 11

Mackenzie River 12
Yukon River 13
Ob River 14
Yenisei River 15
Lena River 16
Kolyma River 17

III METHODS 18

Sampling 18
Analysis 19
Dissolved Organic Carbon 19
Optical Properties 20
Lignin Phenols 25

IV RESULTS 30

Yukon River 30
Dissolved Organic Carbon (DOC) 30
Optical Properties 30

CHAPTER Page

Lignin Phenols 40
Mackenzie River 45
Dissolved Organic Carbon 45
Optical Properties 45
Lignin Phenols 50
Ob River 52
Dissolved Organic Carbon 52
Optical Properties 52
Lignin Phenols 57
Yenisei River 59
Dissolved Organic Carbon 59
Optical Properties 59
Lignin Phenols 61
Lena River 66
Dissolved Organic Carbon 66
Optical Properties 66
Lignin Phenols 71
Kolyma River 73
Dissolved Organic Carbon 73
Optical Properties 73
Lignin Phenols 75

V DISCUSSION AND CONCLUSION 80

Dissolved Organic Carbon 80
Optical Properties 85
Lignin 88
Sorption 96
Conclusion 98

REFERENCES 100

VITA 111

LIST OF FIGURES

FIGURE Page

1 Watershed size and sampling locations (red dots) for the 6 largest Arctic rivers (Ob, Yenisei, Lena, Kolyma, Yukon, and Mackenzie). 11

2 Yukon River discharge ($m^3 s^{-1}$), and a) Dissolved organic carbon (DOC; mg L^{-1}), b) Absorption coefficient at 375 nm (a_{375}; m^{-1}), c) Specific ultraviolet absorption coefficient (SUVA; L(mg OC)$^{-1}$ m^{-1}) and d) Spectral slope (S; μm^{-1}) for the years 2004 and 2005. 31

3 Relationship of Yukon discharge to DOC (mg L^{-1}), spectral slope (μm^{-1}), and SUVA (L (mg OC)$^{-1}$ m^{-1}). 37

4 Fluorescence EEM's measured in Yukon samples from low flow (a,c) and peak flow (b,d) conditions in 2004 (upper panals) and 2005 (lower panals). Note each subplot is on a different scale. 38

5 Seasonal variation in the maximum fluorescence intensity measured at excitation 240 nm (a & c) and 315 nm (b & d) for the Yukon River in 2004 (a & b) and 2005 (c & d). 39

6 Yukon River discharge and a) Sigma 8 (Σ_8; $\mu g L^{-1}$), b) Lambda 8 ($\Lambda 8$; mg LOP (100 mg OC)$^{-1}$, c) Acid to aldehyde ratios for vanillyls and syringyls, d) Syringyls/Vanillyls (S/V) & Cinnamyls/ vanillyls (C/V), e) p-coumaric acid/ferulic acid (CAD/FAD) & p-hydroxybenzaldehyde /total p-hydroxy group (PON/P), f) 3,5-dihydroxybenzoic acid/vanillyl (DiBA/V) & total p-hydroxy group/ (vanillyl + syringyl) (P/(V+S)) 41

7 Mackenzie River discharge ($m^3 s^{-1}$), and a) Dissolved organic carbon (DOC; mg L^{-1}), b) Absorption coefficient at 375 nm (a_{375}; m^{-1}), c) Specific ultraviolet absorption coefficient (SUVA; L(mg OC)$^{-1}$ m^{-1}) and d) Spectral slope (S; μm^{-1}) for the years 2004 and 2005 46

8 Relationship of Mackenzie discharge to DOC (mg L^{-1}), spectral slope (μm^{-1}), and SUVA (L (mg OC)$^{-1}$ m^{-1}) 47

FIGURE Page

9 Fluorescence EEM's measured in Mackenzie samples from low flow (a,c) and peak flow (b,d) conditions in 2004 (upper panals) and 2005 (lower panals). Note each subplot is on a different scale..... 48

10 Seasonal variation in the maximum fluorescence intensity measured at excitation 240 nm (a & c) and 315 nm (b & d) for the Mackenzie River in 2004 (a & b) and 2005 (c & d). 49

11 Mackenzie River discharge and a) Sigma 8 (Σ_8; μg L^{-1}), b) Lambda 8 (Λ8; mg LOP (100 mg OC)$^{-1}$, c) Acid to aldehyde ratios for vanillyls and syringyls, d) Syringyls/Vanillyls (S/V) & Cinnamyls/ vanillyls (C/V), e) p-coumaric acid/ferulic acid (CAD/FAD) & p-hydroxybenzaldehyde/total p-hydroxy group (PON/P), f) 3,5-dihydroxybenzoic acid/vanillyl (DiBA/V) & total p-hydroxy group/ (vanillyl + syringyl) (P/(V+S))..... 51

12 Ob River discharge (m^3 s^{-1}), and a) Dissolved organic carbon (DOC; mg L^{-1}), b) Absorption coefficient at 375 nm (a_{375}; m^{-1}), c) Specific ultraviolet absorption coefficient (SUVA; L(mg OC)$^{-1}$ m^{-1}) and d) Spectral slope (S; μm^{-1}) for the years 2004 and 2005 53

13 Relationship of Ob discharge to DOC (mg L^{-1}), spectral slope (μm^{-1}), and SUVA (L (mg OC)$^{-1}$ m^{-1}). 54

14 luorescence EEM's measured in Ob samples from low flow (a,c) and peak flow (b,d) conditions in 2004 (upper panals) and 2005 (lower panals). Note each subplot is on a different scale..... 55

15 Seasonal variation in the maximum fluorescence intensity measured at excitation 240 nm (a & c) and 315 nm (b & d) for the Ob River in 2004 (a & b) and 2005 (c & d). 56

16 Ob River discharge and a) Sigma 8 (Σ_8; μg L^{-1}), b) Lambda 8 (Λ8; mg LOP (100 mg OC)$^{-1}$, c) Acid to aldehyde ratios for vanillyls and syringyls, d) Syringyls/Vanillyls (S/V) & Cinnamyls/ vanillyls (C/V), e) p-coumaric acid/ferulic acid (CAD/FAD) & p-hydroxybenzaldehyde/total p-hydroxy group (PON/P), f) 3,5-dihydroxybenzoic acid/vanillyl (DiBA/V) & total p-hydroxy group/(vanillyl + syringyl) (P/(V+S)) 58

FIGURE Page

17 Yenisei River discharge ($m^3 s^{-1}$), and a) Dissolved organic carbon (DOC; mg L^{-1}), b) Absorption coefficient at 375 nm (a_{375}; m^{-1}), c) Specific ultraviolet absorption coefficient (SUVA; L(mg OC)$^{-1}$ m^{-1}) and d) Spectral slope (S; μm^{-1}) for the years 2004 and 2005 60

18 Relationship of Yenisei discharge to DOC (mg L^{-1}), spectral slope (μm^{-1}), and SUVA (L (mg OC)$^{-1}$ m^{-1}). 61

19 Fluorescence EEM's measured in Yenisei samples from low flow (a,c) and peak flow (b,d) conditions in 2004 (upper panals) and 2005 (lower panals). Note each subplot is on a different scale 62

20 Seasonal variation in the maximum fluorescence intensity measured at excitation 240 nm (a & c) and 315 nm (b & d) for the Yenisei River in 2004 (a & b) and 2005 (c & d). 63

21 Yenisei River discharge and a) Sigma 8 (Σ_8; $\mu g L^{-1}$), b) Lambda 8 ($\Lambda 8$; mg LOP (100 mg OC)$^{-1}$, c) Acid to aldehyde ratios for vanillyls and syringyls, d) Syringyls/Vanillyls (S/V) & Cinnamyls/ vanillyls (C/V), e) p-coumaric acid/ferulic acid (CAD/FAD) & p-hydroxybenzaldehyde/total p-hydroxy group (PON/P), f) 3,5-dihydroxybenzoic acid/vanillyl (DiBA/V) & total p-hydroxy group/ (vanillyl + syringyl) (P/(V+S)) 65

22 Lena River discharge ($m^3 s^{-1}$), and a) Dissolved organic carbon (DOC; mg L^{-1}), b) Absorption coefficient at 375 nm (a_{375}; m^{-1}), c) Specific ultraviolet absorption coefficient (SUVA; L(mg OC)$^{-1}$ m^{-1}) and d) Spectral slope (S; μm^{-1}) for the years 2004 and 2005 67

23 Relationship of Lena discharge to DOC (mg L^{-1}), spectral slope (μm^{-1}), and SUVA (L (mg OC)$^{-1}$ m^{-1}). 68

24 Fluorescence EEM's measured in Lena samples from low flow (a,c) and peak flow (b,d) conditions in 2004 (upper panals) and 2005 (lower panals). Note each subplot is on a different scale 69

25 Seasonal variation in the maximum fluorescence intensity measured at excitation 240 nm (a & c) and 315 nm (b & d) for the Lena River in 2004 (a & b) and 2005 (c & d). 70

FIGURE Page

26 Lena River discharge and a) Sigma 8 (Σ_8; μg L^{-1}), b) Lambda 8 (Λ8; mg LOP (100 mg OC)$^{-1}$, c) Acid to aldehyde ratios for vanillyls and syringyls, d) Syringyls/Vanillyls (S/V) & Cinnamyls/ vanillyls (C/V), e) p-coumaric acid/ferulic acid (CAD/FAD) & p-Hydroxybenzaldehyde/ total p-hydroxy group (PON/P), f) 3,5-dihydroxybenzoic acid/vanillyl (DiBA/V) & total p-hydroxy group/ (vanillyl + syringyl) (P/(V+S)) 72

27 Kolyma River discharge (m^3 s^{-1}), and a) Dissolved organic carbon (DOC; mg L^{-1}), b) Absorption coefficient at 375 nm (a_{375}; m^{-1}), c) Specific ultraviolet absorption coefficient (SUVA; L(mg OC)$^{-1}$ m^{-1}) and d) Spectral slope (S; μm^{-1}) for the years 2004 and 2005 74

28 Relationship of discharge to DOC (mg L^{-1}), spectral slope (μm^{-1}), and SUVA (L (mg OC)$^{-1}$ m^{-1}). 75

29 Fluorescence EEM's measured in Kolyma samples from low flow (a,c) and peak flow (b,d) conditions in 2004 (upper panals) and 2005 (lower panals). Note each subplot is on a different scale 76

30 Seasonal variation in the maximum fluorescence intensity measured at excitation 240 nm (a & c) and 315 nm (b & d) for the Kolyma River in 2004 (a & b) and 2005 (c & d). 77

31 Kolyma River discharge and a) Sigma 8 (Σ_8; μg L^{-1}), b) Lambda 8 (Λ8; mg LOP (100 mg OC)$^{-1}$, c) Acid to aldehyde ratios for vanillyls and syringyls, d) Syringyls/Vanillyls (S/V) & Cinnamyls/ vanillyls (C/V), e) p-coumaric acid/ferulic acid (CAD/FAD) & p-hydroxybenzaldehyde/total p-hydroxy group (PON/P), f) 3,5-dihydroxybenzoic acid/vanillyl (DiBA/V) & total p-hydroxy group/ (vanillyl + syringyl) (P/(V+S)) 79

32 The average (2004 and 2005) DOC export (Tg yr^{-1}) for the Mackenzie,Yukon, Yenisei, Lena, Ob and Kolyma and a) river discharge (km^3 yr^{-1}), b) river length (km) and c) catchment area (10^6 km^2) 82

33 The relationship between Absorption coefficient at 375 nm and DOC data for all rivers, all seasons 86

FIGURE Page

34 Relationship between lignin yield (Λ8) and ratio of vanillic acid/ vanillin ((ad/al)v). a) all river data divided by hydrologic state, b) river to river comparison 90

35 Comparison of cinnmyls/vanillyls (C/V) to syringyls/vanillyls (S/V). a) All river data divided by hydrologic state and b) river to river comparison. Highlighted regions show the composition of various plant material of according to Hedges and Mann (1979). (A)-woody angiosperms, (a)-non-woody angiosperms, (G)-woody gymnosperms and (g)-non-woody gymnosperms. c) expansion of x and y axis from subplot b 92

36 The relationship between C/V and S/V divided into different hydrological states for the a) Ob and b) Kolyma Rivers 94

LIST OF TABLES

TABLE Page

1 Physical data for Mackenzie, Yukon, Ob, Yenisei, Lena and Kolyma Rivers including discharge, order, watershed size, length, mean slope, mean elevation, maximum elevations and extent of continuous permafrost taken from Brabets et al. (2000), Vörösmarty et al. (2000), Gordeev. (2006), Zhang et al. (1999). 13

2 Sampling locations and gauging stations including latitude and longitude coordinates, for rivers investigated in PARTNERS project.... 19

3 Retention times (RT; min) and ions used to identify lignin oxidation products. The ion in italics was used for quantification. LOP grouped into vanillyl, syringyl, cinnamyl and p-hydroxy 28

4 Lignin parameter data from one NIST sediment standard generated using the Thermo Finnegan Trace GC-Polaris Q mass spectrometer and the Varian 3800/4000 GC/MS. (Σ8= Sum of LOP μg/L, Λ8=mg LOP/100 mg OC, S/V=syringyls/vanillyls, C/V=cinnamyls/vanillyls, $(ad/al)_v$ = the ratio of vanillic acid to acetovanillone, DiBA/V=3,5 Dihydroxybenzoic acid/vanillyls, P/(P+S)= total *p*-hydroxy group/ (*p*-hydroxy group+Syringyl), PON/P =*p*-Hydroxyacetophenone/ total *p*-hydroxy group, CAD/FAD=*p*-coumaric acid/ferulic acid)..... 29

5 Seasonal data from all rivers including sample date, discharge, DOC, S, SUVA, a_{375}. Discharge data for the Yukon was generated by USGS, Mackenzie by Water Survey of Canada, and the Ob, Yenisei, Lena and Kolyma by The State Hydrological Institute in St. Petersburg, Russia. 32

6 Estimated annual dissolved organic carbon (DOC) export for 2004 and 2005. DOC is presented as the discharge weighted annual mean DOC concentration (mg L^{-1}), the annual estimated DOC export (Tg yr^{-1}) as well as the area weighted DOC export (kg DOC km^{-2} yr^{-1}) 35

7 Seasonal data from all rivers including sample date, discharge, Σ8, Λ8, S/V, C/V, $(ad/al)_v$, DiBA/V, P/(V+S), PON/P, CAD/FAD. Discharge data for the Yukon was generated by USGS, Mackenzie by Water Survey of Canada, and the Ob, Yenisei, Lena and Kolyma by The State Hydrological Institute in St. Petersburg, Russia..... 42

CHAPTER I

INTRODUCTION

Climate change is gaining momentum as the focus of much of the current Arctic research. The Arctic Climate Impact Assessment (ACIA) released in 2005 addressed many potential affects of global temperature increases on the Arctic environment and how the Arctic may serve as a feedback loop to climate change. The complexity of the environment requires much more research before any conclusions can be made, however, it is clear the Arctic is changing far more rapidly than the rest of the planet. The Intergovernmental Panel on Climate Change (IPCC) (2001) reported an increase in the average global surface air temperature of 0.6 ± 0.2ºC during this century and project by 2100, temperatures will rise between 1.4 and 5.8ºC. In addition, reports of rising temperatures over parts of the Arctic are almost twice that of the rest of the planet (ACIA, 2005). Changes in the hydrological cycle and thermal permafrost degradation are among the many processes potentially altered by increasing atmospheric temperatures.

The Arctic holds a prominent role in the global hydrological cycle, hence has a major influence on climatic conditions. The outflow of relatively fresh surface water from the Arctic Ocean is an important factor in North Atlantic Deep Water (NADW) formation (Broecker, 1997). This process is partially responsible for the modulation of our climate; therefore as these water masses freshen, NADW formation will likely be affected (Peterson et al. 2002; and ref therein). The freshwater balance of the Arctic Ocean is determined by several different inputs: precipitation, river discharge, glacier melt, and sea ice thaw. Each of these inputs is intimately affected by temperature and will become a major concern as our planet warms.

Theoretical arguments and models have both suggested that as atmospheric temperatures increase so will precipitation over the high latitudes (ACIA and ref therein, 2005). Precipitation is difficult to measure in this region because the remoteness and

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This thesis follows the style of *Limnology and Oceanography*.

extreme climate make it impossible for most types of monitoring. However, the ACIA (2005) uses satellite data and models that project an increase of net atmospheric moistureinput (precipitation minus evaporation) of between 6-12% over the Arctic watersheds by the end of the 21st century. This agrees with the work of Curry et al. (2003) who have also shown increased precipitation rates over parts of the Arctic. Another study (Serreze et al. 2000) showed general increases in precipitation over the Arctic region, with the largest increases occurring during fall and winter. In theory, river discharge will also increase as precipitation does over this region, though this may not always be the case. New et al (2000) show that over the Yenisei and Lena watersheds precipitation rates are decreasing. However, river discharge has increased, which may be explained by melting permafrost. Increased river discharge to the Arctic Ocean is important because these rivers supply 10% of the global river discharge. Peterson et al. (2002) used historical records to show that Eurasian river discharge is increasing by 0.007 sverdrup/ºC. Assuming a Surface Air Temperature (SAT) rise of 1.4 to 5.8ºC (IPCC, 2001) by 2100, river discharge to the Arctic Ocean will increase by 315 to 1260 km^3/yr (Peterson et al. 2002). One interesting aspect of these changes is how they are integrated with the seasonal cycle. Serreze et al. (2000) showed a trend of increasing air temperature since the mid-1960's over much of the region, however, this trend is amplified during winter and spring compared to summer. Glacier melt and sea ice thaw are beyond the scope of this project and will not be discussed in detail except to mention that each has the potential to contribute a significant amount of freshwater to the Arctic Ocean. Small glaciers in Alaska, Canada, and Svalbard generally have negative cumulative balances (shrinking) and are responsible for 20% of the global sea level rise since 1961 (Serreze et al. 2000). In the last decade Greenland glacier melt has accelerated from approximately 90 km^3/year to 224 km^3/year (Rignot and Kanagaratnam 2006). Finally, sea ice extent has decreased by $2.9 \pm 0.4\%$ per decade and is accompanied by an increase in the length of ice melt season (Serreze et al. 2000).

Permafrost thaw will make a large contribution to the global carbon budget; however, the fate of this carbon is unknown. Permafrost is defined as being perenially

frozen for 2 consecutive years, therefore its distribution is confined to severe climatic conditions. Because permafrost is frozen, organic material is isolated from degradation processes (UV and microbial) indicating it has a great capacity to store organic carbon. McGuire et al. (1995) determined that approximately 40% of globally reactive soil organic carbon stock is located in the Arctic Region. Lachenbruch and Marshall (1986) showed that surface permafrost temperatures have increased 2-4ºC in northern Alaska during the 20^{th} century. Others (Pavlov, 1994; and Osterkamp and Romanovsky 1999) have also indicated patches of permafrost warming and thawing as well as increased active layer depth (Oelke et al. 2004; Stendel and Christensen 2002). As a result of this change vast stores of organic matter potentially, able to support heterotrophic consumption, could become available. Increasing SAT cannot entirely account for permafrost thaw which is also most likely influenced by changes in snow and vegetative coverage (Serreze et al. 2000). Right now research indicates the Siberian Arctic is a sink for CO_2 (Smith et al. 2004; Stolbovoi 2002), whereas Alaska is a source (Serreze et al. 2000 and ref therein). The presence of higher concentrations of bioavailable organic matter as a result of thawing permafrost may fuel a positive feedback loop by increased production of CO_2 and CH_4 (Goulden et al. 1998; Smith et al. 2004). A couple of recent studies have shown the potential of permafrost to dynamically alter the carbon budget of the Arctic. In a study (Walter et al. 2006) conducted in thermokarst lakes, which are formed when ice within permafrost thaws, measured CH_4 fluxes of 3.8 teragrams yr^{-1}. These measurements increase the present estimates by 10-63%. Another study (Zimov et al. 2006) on yedoma (permafrost with an excess of windblown dust from glacial times) in Siberia showed respiration rates of initially 10 to 40 g of carbon per m^3 per day that reduce to 0.5 to 5 g of carbon per m^3 per day for the next several years. The former 2 studies have both shown that the organic matter released from thawing permafrost is highly biodegradable; therefore its release will significantly alter the carbon budget of our planet.

While gaseous emissions of methane seem to be derived from thermally degraded permafrost (Walter et al. 2006; Zimov et al. 2006), it is unclear how influential

this process is to the dissolved organic matter (DOM) composition in the Arctic rivers. As the hydrology of the region changes as discussed above there could be an increased flux of terrestrial dissolved organic matter (TDOM) to the Arctic Ocean (Tranvik and Jansson 2002). Benner et al. (2004) and Amon and Meon (2004) both reported modern radiocarbon dates in ultrafiltrated dissolved organic matter (UDOM) from western Siberian and Alaskan rivers, indicating the source of UDOM is currently not from permafrost degradation. Guo and Macdonald (2006) showed that POC from the Yukon River was derived from relict carbon while DOC was contemporary. It is likely that the dissolved material is derived from surface run-off (leaching) whereas particulate material is the result of erosional processes. In a recent study on the Kolyma River, Neff et al. (2006) showed that the flux of DOC was overwhelmingly modern, however, late in the season there was a contribution of old carbon aged 675 years BP. In another study (Striegl et al. 2007) on the Yukon, radiocarbon ages of 330 years BP was reported on DOC. These contributions of old carbon are small but could be an indication of either cycling of the aged POC or some release of dissolved carbon from permafrost thaw.

The extreme seasonality of the high latitudes makes it difficult to sample in these regions. Regardless of permafrost distribution, from October to early June rivers and soils in the Arctic are frozen, thus little published data exists from this period. While many small streams freeze completely, only the surface of larger streams and rivers freeze, thus base flow is assumed to be supported by groundwater. In the spring when this region experiences longer days, the snow and ice begin to melt causing the rivers to break up. From June to September the rivers discharge 70% of their annual freshwater. The initial flood is surface run-off primarily derived from snowmelt (Hinzman et al. 1991, MacLean et al. 1999, Guo and Macdonald 2006). During this event the soils are still relatively frozen confining runoff to the upper soil horizons (10 cm) (Hinzman et al. 1991). By limiting perculation there is also little opportunity for DOM adsorption by mineral layers; therefore river dissolved organic carbon (DOC) concentrations increase probably reflecting material leached from plant litter (Guo and Macdonald 2006). Work by Finlay et al. (2006) and Guéguen et al. (2006) on the Kolyma and Yukon Rivers,

respectively, provide estimates of ~50-55% of the annual DOC discharge occuring during snowmelt. As temperatures rise, the active layer deepens allowing water to absorb (McNamara et al. 1997) and sorption of DOM to deeper soil horizons depletes DOC concentrations in rivers and streams (MacLean et al. 1999). Flux of DOC therefore follows the hydrological cycle and expansion of the active layer in these watersheds with largest concentrations occurring right at or slightly before peak flow (MacLean et al. 1999, Carey 2003; Guo and Macdonald 2006, and Finlay et al. 2006).

Sorption of DOM to soil mineral horizons is an important mechanism which not only controls the amount of DOC that enters streams or rivers but also alters the composition by preferentially binding some compounds more readily than others. Many sorption studies have shown similar results, as DOM perculates through the soil horizons there is a strong depletion in the dissolved carbon concentration with depth (Cronan and Aiken 1985; Guggenberger and Zech 1994; Kaiser et al. 2004; Kaiser et al. 1996; Kawahigashi et al. 2006; Qualls and Haines 1992). This depletion has been shown to be the result of two processes, microbial degradation and sorption. Degradation is slow in soil and in most cases cannot fully explain the sharp decline in carbon concentrations (Qualls and Haines 1992). Sorption, however, can occur relatively rapidly to Al and Fe-oxides by ligand exchange-suface complexation (Gu et al. 1999), where a metal-associated hydroxyl group is replaced with an organic ligand. It has been found that hydrophobic material having a high aromatic content, rich in carboxylic acids, and has functional groups containing nitrogen and sulfur sorbs most efficiently (Mcknight et al. 1992) to mineral surfaces through these types of chemisorptive processes. Guggenberger et al. (1994) showed that the hydrophobic pool is composed of ~22% lignin , ~30% plant/microbial derived polysaccharides (lignocellulose), and ~25% alkyl substances; while the hydrophilic acids were ~15% lignin, 30% microbial derived polysaccharides, ~25% alkyl substances. The hydrophilic acids also have sorptive properties (Guggenberger et al. 1994), which compete for binding sites with their hydrophobic counterparts (Kaiser et al. 1996).

When OC loading to mineral phases is low (large specific surface area (SSA); juvenile sediments) sorption of both hydrophilic and hydrophobic acids will occur. Often hydrophobic acid ligand exchange will involve several reactive sites making desorption almost impossible and microbial degradation equally difficult especially if it is bound within a micropore (Kaiser and Guggenberger 2003); thus this material for all intents and purposes is preserved. As loading increases, hydrophobic material will sorb preferentially and form stronger interactions (potentially through multiple binding sites) than hydrophilic material. (Kaiser and Zech 1999). Desorption can occur where weaker interactions are made; thus increasing the concentration of hydrophilic material in solution as water passes through the soil layers. At high loading there will also be a possibility for microbial cycling because the OM is only weakly associated. This can be especially important in preferential hydrologic flow paths where nutrients are being replenished; therefore bacteria can efficiently turn over this material by colonizing these minerals (Guggenberger and Kaiser 2003).

Information on the chemical composition of DOM from the Arctic rivers is scarce, and because most sampling occurs during summer or early fall there is even less information on its seasonal dynamics. The only in depth compositional study of this nature was done on the Yukon River (Guo and Macdonald 2006, Guéguen et al. 2006, Zou et al. 2006). The river was sampled 6 times between May and September (encompassing the dynamic hydrograph) at Stevens Village, Alaska. Samples were size fractionated (POM (>0.45 μm), COC (1 kDa-0.45 μm), and LWM-DOC(<1 kDa)) and analyzed for OC, ON, ^{14}C, $\delta^{13}C$, (Guo and Macdonald 2006) absorbance, fluorescence, total dissolved carbohydrates, (Guéguen et al. 2006) and fatty acids (Zou et al. 2006). The various analyses showed interesting differences between size fractions; however, I will discuss COC in greater detail because according to size it is more comparable to the work presented here. The colloidal fraction contributed between 75-85% of the bulk DOC throughout the sampling season (Guéguen et al. 2006). Guo and Macdonald (2006) showed a slight drop in colloidal C/N during peak flow (avg 45.8 ± 3.2, peak flow=42.9) while $\delta^{13}C$ remained constant (avg -27.44±0.19). Both high C/N ratios and

$\delta^{13}C$ indicate highly aromatic organic matter likely of vascular plant origin. The slight drop in C/N during peak flow may point to less humified OM during peak flow relative to base flow (See and Bronk 2005; Guo and Macdonald 2006); however, due to the error surrounding the measurement its hard to argue these values are different. Spectral slopes for COC do not change throughout the season, however, both HMW and LMW increase from peak flow to base flow (Guéguen et al. 2003) indicating during the ice free period OM becomes more degraded (Stedmon and Markager 2001). Fluorescence measurements indicate a red shift in the emission maximum of COC by 5 nm, which Guéguen et al. (2006) interpret as a reduction of molecular weight with progression of the season. Carbohydrates contributed about 25% of the total DOC, with 85±4% of the carbohydrates in the COC pool (Guéguen et al. 2006), remaining relatively constant during the sampling period. The ratios of mucopolysaccharides/total carbohydrates (MCHO/TCHO) and polysaccharides/total carbohydrates (PCHO/TCHO) changed slightly indicating during the ice free time there is a potential microbial transformation of the carbon pool (Guéguen et al. 2006). Short chained saturated (14:0, 16:0, and 18:0) and monounsaturated (16:1, and 18:1) fatty acids contributed 70-80% of fatty acid pool regardless of organic matter size pool and sampling time (Zou et al. 2006). Bacterial fatty acids (normal and branched 15:0 and 17:0 plus 18:1) contributed a smaller (~16-30%), but substantial, portion of the total fatty acid pool with abundances increasing during the ice open season (Zou et al. 2006). Fatty acids compositions suggest that land derived material dominated during river break-up while aquatically produced DOM (though minor) peaks in July, this is supported by a peak in Chlorophyll *a* during this period (Zou et al. 2006).

Similar C/N (48.7 and 42.7) and $\delta^{13}C$ (-27.1 and -27.7) were reported by Amon and Meon (2004) for UDOM in the Yenisei and Ob Rivers, respectively. Lara et al. (1998) sampled 18 stations along the Lena River and found slightly higher but comparable C/N ratios (30-58; with 75% of the values 45-55) for bulk DOM. These values for Siberian Rivers suggest a common highly aromatic vascular plant origin, despite the spatial differences between rivers.

Studies using optical properties such as fluorescence or UV-Vis absorbance are equally rare on Arctic Rivers. Amon et al. (2003) used 3D excitation-emission matrices (EEM's) from the Mackenzie, Yenisei, and Ob Rivers to identify and understand mixing of water masses that are supported by rivers in the Arctic Ocean. These EEM's all show a similar fluorescence pattern with 2 regions of high intensity described as humic peaks A and C, located at Ex: 270 Em: 455 and Ex: 320-325 Em: 435-445. In another study on the Yukon River, Specific Ultraviolet Absorption Coefficients (SUVA) along with chromatographic separation using XAD resins were used to describe seasonal DOM compositional changes (Striegl et al. 2005). During the wintertime, Striegl et al. (2005) show that DOM is less aromatic (low SUVA) and hydrophobic and has a lower C/N. In contrast, at peak flow DOM is very aromatic (high SUVA) is largely hydrophobic material and has a very high C/N.

The only other study using optical properties comparable to the work presented here was conducted by Gueguen et al. (2006) and was reported above. Lignin being an unambiguous biomarker for vascular plants can be a useful property to investigate origin, transport and cycling of terrestrial DOM in the environment (Dalzell et al. 2005; Ertel and Hedges 1984; Guggenberger and Zech 1994; Houel et al. 2006; Opsahl and Benner 1995; Opsahl and Benner 1998; Opsahl et al. 1999). The vanillyl (V), syringyl (S), cinnamyl (C), and p-hydroxyl (P), groups of lignin oxidation products (LOP) are often quantified and used to describe source and degradation state of OM. In each group, with the exception of the cinnamyls, there is an acid, aldehyde and ketone identified. Lignin compositions determined on UDOM from the Yenisei (S/V=0.33) and Ob (S/V=0.46) Rivers show a predominately gymnosperm origin (low S/V) reflecting the vast Siberian boreal forest influencing the watersheds (Opsahl et al. 1999). Low S/V values were also reported by Lobbes et al. (2000) for DOM (<0.7 μm) in the Yenisei (0.11), Lena (0.19) and Kolyma (0.31) Rivers. The Lobbes et al. (2000) study shows slightly lower values than the work of Opsahl et al. (1999), which may be attributed to differing methodologies or size fractions. Degradation state is often described using the ratio of vanillin to vanillic acid (Hedges et al. 1988a); however, it can also reflect

leaching (Hedges and Weliky 1989) or sorption (Kawahigashi et al. 2006). (Ad/Al)v range from 1.12-1.50 in the Yenisei River and 1.14-1.47 for the Ob River (Opsahl et al. 1999).

Seasonal studies where lignin compositions are reported are limited to rivers in lower latitudes. Work on the Pearl River (Duan et al. 2007), a blackwater river in Mississippi, showed more lignin mobilized (Λ_8; mg LOP/100 mg Organic Carbon) with a higher diagenetic age ((ad/al)v) during high discharge compared to low. During base flow the authors suggest there is more time for sorption of lignin to soil layers, further the OM shows a 'fresher' quality because of preferential sorption of the lignin acidic side chains to deeper mineral layers. In contrast, during flood events more leaching of surface litter increases the total amount of lignin and the (ad/al)v. This seems contrary to what would be expected given that baseflow is generally supported by ground water and/or seepage from deeper soil layers where longer residence times might enhance microbial processes. OM composition might then reflect the higher decomposition occurring in these deeper layers. This is the case in another study conducted on the agriculturally dominated Big Pine Creek in central Indiana (Dalzell et al. 2005). The authors size fractionated samples into HMW-DOC (1 kDa-0.2 μm), COC (0.2 μm-0.7 μm), and POC (>0.7 μm). All size fractions showed increased export of lignin (Λ_8) during flood events, but only the HMW-DOC (ad/al)v decreased from baseflow to flood events (fresher material during flood; Dalzell et al. 2005). The POC and COC fractions showed no significant differences between hydrologic periods indicating that the fractions have different sources. Seasonal lignin compositions from the Mississippi River (Duan et al. 2007) show no change in (ad/al)v between hydrologic events. OM composition in this large watershed is influenced by many processes including vegetation diversity, soil decomposition, climatic events, and anthropogenic activities (agriculture; Duan et al. 2007). These processes probably contribute to the more integrated seasonal signal found in this large river. Differences in (ad/al)v trends between rivers support the fact that watershed characteristics have an important impact on DOC cycling and export to rivers and streams.

As the result of climate change observations and the influence of the Arctic on global conditions, it became apparent that a large-scale study needed to be conducted on the rivers of this region. In 2002, the National Science Foundation funded a multi-disciplinary and multi-national group of researchers led by Dr. Bruce Peterson at the Marine Biological Laboratory for this task. The main objective of the PARTNERS (Biogeochemical Tracers in Arctic Rivers: Linking the Pan-Arctic watershed to the Arctic Ocean) research is to understand the seasonal differences in the 6 largest Arctic Rivers (Ob, Yenisei, Lena, Kolyma, Yukon, and Mackenzie) using various inorganic and organic tracers. These measurements include salinity, pH, dissolved oxygen, $H_2{}^{18}O$, barium, nutrients (NO_3^-, NH_4^+, PO_4^{3-}, SiO_2) , major ions (Cl^- SO_4^-, Mg^{2+}, Ca^{2+}, Na^-, K^+, F^-) alkalinity, ^{14}C (POC, DOC, DIC), and ^{13}C (POC, DOC, DIC). One goal was to establish a baseline for organic and inorganic matter discharge to gauge the magnitude of future environmental change in those rivers. Our focus in the PARTNERS project included the investigation of the optical properties and lignin phenol composition of dissolved organic matter (DOM) discharged by those rivers over several seasonal cycles. In this thesis I will address the following questions:

1. How does the chemical composition of DOM differ among the 6 largest Arctic Rivers (Yukon, Mackenzie, Ob, Yenisei, Lena, and Kolyma?
2. How does chemical composition of DOM change over annual cycle?
3. How is DOM quality linked to watershed characteristics?

CHAPTER II

STUDY SITE

The distribution and size of watersheds supporting the six largest Arctic Rivers are shown in Figure 1, with the red dot indicating the approximate sampling location. Of these six rivers, four are located in Siberia (Ob, Yenisei, Lena and Kolyma), and two in North America (Mackenzie, and Yukon). Climate determines the extreme hydrological

Figure 1. Watershed size and sampling locations (red dots) for the six largest Arctic rivers (Ob, Yenisei, Lena, Kolyma, Yukon, and Mackenzie).

regime which causes surface freezing during the winter. Generally, the rivers begin to thaw in May and experience freshet in early June. Between June and September ~70% of annual discharge occurs, by October surface freezing commences. Permafrost distribution is also determined by climate. With the exception of the Kolyma, the northernmost part of each watershed is continuous permafrost, and degrades to discontinuous then sporadic to the south. The Kolyma River, is entirely above 60° N and experiences the coldest climate conditions hence it is completely underlain by continuous permafrost.

Mackenzie River

The Mackenzie River is the forth largest river in terms of discharge (3.3×10^{11} m^3 yr^{-1}) (Gordeev. 2006) draining into the Arctic Ocean. Its watershed is 1.713×10^6 km^2 and begins near the Great Slave Lake in the Northwest Territories of Canada and extends to the Beaufort Sea. Table 1 presents physical data (discharge, order, catchment size, river length, mean slope, mean elevation, maximum elevation and extent of continuous permafrost) from Brabets et al. (2000), Vörösmarty et al. (2000), Gordeev. (2006) and Yang et al. (2002) for all six rivers. The Mackenzie supplies the Beaufort Sea with approximately 1.3×10^6 tons of dissolved organic carbon (DOC) per year (Goni et al. 2000) in a similar seasonal trend as discharge. Though discontinuous to sporadic permafrost is found to a large extent within of the basin, continuous permafrost is only located in relatively small region in the north (~20-30%; Zhang et al. 1999). Sedimentary bedrock underlying the catchment consists of carbonates, shales, siltstones, mudstones and till is the dominant parent material (Timoney et al. 1993). Soils are typically Orthic Regosols, and Gleysolic Turbic Cryosols in the north (Timoney et al. 1993) with luvisols and podsols in the south (Mackenzie River Basin Board, MRBB). Vegetation can be determined by any number of variables including soil pH, moisture content, exposure and temperature (Timoney 1993). Vegetation in the north consists of treeless tussock tundra with the dominant groups being legumes, carices and mosses

(*Arctostaphylos rubra, Dryas integrifolia, Hedysarum alpinum, Lupinus arcticus, Ditrichum flexicaule*) (Timoney et al 1993). Boreal coniferous forest dominates the southern parts of the watershed with mainly white spruce (*Picea glauca*) in the north and black spruce (*Picea mariana*) in the south (Goni et al 2000).

Table 1. Physical data for Mackenzie, Yukon, Ob, Yenisei, Lena and Kolyma rivers including discharge, order, watershed size, length, mean slope, mean elevation, maximum elevations and extent of continuous permafrost taken from Brabets et al. (2000), Vörösmarty et al. (2000), Gordeev. (2006), Zhang et al. (1999).

River	Discharge (10^{11} m^3)	Order	Catchment size (10^6 km^2)	Length (km)	Mean slope (m km^{-1})	Mean Elev. (m)	Max Elev. (m)	Continuous Permafrost (%)
Yenisei	6.20	5	2.582	4803	1.94	670	3500	35-55
Ob	4.04	5	2.570	3977	1.28	270	4280	4-10
Lena	5.23	6	2.418	4387	1.83	560	2830	78-93
Mackenzie	3.30	5	1.713	3679	2.23	590	3350	20-30
Yukon	2.00	5	0.852	2716	2.93	690	6100	16
Kolyma	1.22	4	0.666	2091	2.16	490	2560	100

Yukon River

The Yukon River in Alaska is the forth largest river in North America, its discharge totals 2.0 x 10^{11} m^3 annually and drainage basin covers 0.855 x 10^6 km^2 (Table 1). Of the six rivers studied in this project this is the only one that drains into the Bering Sea instead of the Arctic Ocean. The Yukon discharges 1.58 x 10^6 t of DOC per year (Striegl et al. 2007). The watershed is situated between the Central and Eastern Brooks Range in the north and the Alaska Range and Wrangell-St. Elias Mountains to the south. The source of the river is unclear but it is believed to initiate from the Llewellyn Glacier near the Atlin Lake in British Columbia (Brabets et al. 2000). The mountainous terrain creates a steeper mean slope (2.93 m km^{-1}), higher mean elevation (690 m) and higher maximum elevation (6100 m) (Table 1) than the other rivers studied here. The Yukon is underlain with 16% continuous permafrost (Brabets et al. 2000). Geology for the Yukon is very complex and reflects the active tectonic activity of the region (Brabets et

al. 2000). Generally, the age of rocks range from Precambrian to Holocene and are composed of unconsolidated deposits and consolidated rocks (Brabets et al. 2000). Sedimentary rocks are primarily composed of sandstone, siltstone, shale and limestone but certain locations can contain smaller amounts of coal, mudstone, conglomerate, dolomite and chert (Brabets et al. 2000). Volcanic rocks have a variable composition ranging from rhyolite, andesite, basalt, sandstone, and chert (Brabets et al. 2000). Paleozoic metamorphic rocks are present over much of the Yukon-Tanana upland and are composed of gneiss, schist, phyllite, and quartzite (Brabets et al. 2000). The most abundant soil types within the Yukon watershed are cryosols and inceptisols (cambisols) with minor amounts of regosols, inceptosols/gelisols and mollisols (Brabets et al. 2000). Approximately 53% of the catchment is covered by spruce forest, white (*Picea glauca*) in well drained sites and black (*Picea mariana*) in lowland sites (Brabets et al. 2000). Another 40% is divided almost equally between shrubland (alders and willows), broadleaf forest (white birch and balsam), lichens, wet herbaceous (grasslands) and barren (lichens if any vegetation) (Brabets et al. 2000). About 6% is separated into dwarf birch and sedges (Brabets et al. 2000). Finally about 3%, mostly located within the Alaska Range and Wangell-St. Elias Mountains, is covered by ice, snow and water (Brabets et al. 2000).

Ob River

The Ob River is the westernmost of the Siberian rivers studied in this project. Its discharge totals 4.04×10^{11} m^3 yr^{-1} or 15% of total freshwater flow into Arctic Ocean and drainage basin is approximately 2.57×10^6 km^2 (Table 1). DOC discharge totals 3.68×10^6 tons yr^{-1} (Rachold et al. 2004). Of the Siberian rivers studied herein it experiences the mildest climate therefore has the least amount of continuous permafrost (4-10%) within its catchment (Zhang et al. 1999). The source of this river is in the Altai mountains and extends to the Kara Sea with a total length of 3977 km. Most of the lower reaches of the catchment are relatively flat with altitudes of 50-150 m (Stolbovoi et al. 1998) and slopes between 0-2% (Stolbovoi et al. 1998) which creates enormous

flood plains. The mountainous region of the upper river has elevations ~4000 m and a steeper slope (30-60%) (Stolbovoi et al. 1998) creating an average slope of 1.28 m km^{-1} (Table 1). Compared to the Yenisei and Lena its catchment is the most populated, and is more influenced by industrial activities and agricultural development (Yang et al. 2004). The geology includes granites, clayey sandstone and limestones (Gordeev. 2004). Soils are mainly cryosols, histosols, podzoluvisols, and podsols (Stolbovoi et al. 1998). The Ob is unique among the other five rivers because it contains within its watershed the largest peat bog system on our planet. The western Siberian lowlands are 900,000 km^2 (Kremenetski et al. 2003) and are a recognized source of methane for our planet (Smith et al. 2004). Vegetation is variable in this watershed compared with the others because of its milder climate but forests include larch, pine and birch species (Wagner 1997) with sphagnum mosses being dominant in the peat bog as well as lesser amounts of shrubs, grasses and sedges (Opsahl et al. 1999; and ref therein). Compared to other rivers the Ob is notable for its abundance of angiosperm vegetation due to milder climate.

Yenisei River

The Yenisei is the longest (4803 km), has the greatest discharge (6.2 x 10^{11} m^3 yr^{-1}) and largest watershed (2.6 x 10^6 km^2) of all Arctic Rivers (Table 1). DOC discharge from the Yenisei is the largest of all the Arctic Rivers totaling 4.86 x 10^6 t yr^{-1} (Rachold et al. 2004). The source of this river is the Baikal mountains in south Central Siberian Plateau, and along with the Ob flows north into the Kara Sea through the Central Siberian Uplands. The mean elevation is 670 m and average slope is 1.94 m km^{-1} (Table 1). Both elevation and slope classes are variable throughout the watershed but gradually increase nearing the Baikal mountains. Soils include cryosols, podsols, inceptisols, podzoluvsols and leptosols (Stolbovoi et al. 1998). The climate is more severe than the Ob therefore 36-55% of its watershed is underlain with continuous permafrost (Zhang et al. 1999). Vegetation varies from tundra, mixed taiga and pine forest from north to south. The tundra is mainly dwarf birch (*Betula nana)*, sedges (*Carex canescens, Eriophorum vaginatum*) and mosses (*Hylocomium proliferum*,

Polytrichum commune and *Sphagnum spp.)* (Šantrůčková et al. 2003). Mixed taiga may include spruce (*Picea obovata*), larch (*Larix sibirica)* birch (*Betula sp.*) and pine *(Pinus sibirica*) as the dominant species and any number of subdominant plants including horsetails (*Equisetum pretense* and *E. sylvaticum),* berries (*Rubus arcticus* and *R. chamaemorus)*, and mosses (*Hylocomium proliferum*, *Cladonia spp.*, and *Sphagnum spp.;* Šantrůčková et al. 2003). In the south there is a transition into Scots pine forests (*Pinus sylvestris;* Šantrůčková et al. 2003).

Lena River

The Lena is the second largest Arctic River in terms of discharge (5.23×10^{11} m^3 yr^{-1}) (Table 1) and provides the Laptev sea with 3.6×10^6 t of DOC per year (Rachold et al. 2004). The river is bounded by the Baikal Mountains in the south, the Verkhoyansk Ridge to the east, the Central Siberian Uplands in the west and flows into Laptev Sea through a complex braided network of channels. Total length of the river is 4387 m with its watershed covering 2.418×10^6 km^2 (Table 1). The catchment's average slope is 1.83 m km^{-1}, and mean and maximum elevations are 560 and 2830 m, respectively (Table 1). Continuous permafrost underlies 78-93% of the watershed (Zhang et al. 1999) extending down to 50° N. The geology of the northern to middle watershed is mostly Cambrian and Precambrian limestones, with Jurassic to Cretaceous aged terrigenous sediments and Quaternary alluvial deposits (Rachold 1999). The southern parts of the watershed is composed of Proterozoic gneiss, shists, quartzites, and marbleized limestones (Rachold 1999). Soils are mainly leptosols, podsols, and inceptisols with minor amounts of

fluvisols, cryosols, and podzoluvisols (Stolbovoi et al. 1998). Severe climate limits the growth of most species this region except larch forests (*Larix gmelinii and L. cajanderi)* which occupy much of the watershed (Wagner 1997). To the south where conditions are less severe pine and birch forests are present (Wagner 1997).

Kolyma River

The Kolyma is the smallest of the rivers studied in this project. Its discharge totals 1.22×10^{11} m^3 annually and drains 0.67×10^6 km^2 (Table 1) underlain entirely by continuous permafrost. The Kolyma has the lowest dissolved carbon discharge of the rivers studied here totaling 0.96×10^6 t per year (Finlay et al. 2006). It is the easternmost Siberian river and is bounded by the Kolyma Mountains to the southeast and the Chersky Ridge to the southwest. The average slope is 2.16 m km^{-1}, and mean and maximum elevations are 490 and 2560 m, respectively (Table 1). Soils include cryosols, inceptosols, podsols, and histosols (Stolbovoi et al. 1998). Vegetation is limited to larch forests (*Larix gmelinii and L. cajanderi)* which dominate the entire watershed (Wagner 1997).

CHAPTER III

METHODS

Sampling

The project was coordinated by a core group at Marine Biological Laboratory (MBL) in Woods Hole, MA. Sampling times and frequencies were planned by this core group and executed by local agencies proximate to each river. The agencies were contracted to collect samples and conduct initial filtration/preservation of samples before shipment to MBL. At the end of each season frozen samples were shipped to involved principal investigators.

Samples used for this study were collected during the years 2004-2005. Discharge data has been recorded from a gauging station since 1936 for the Ob, Yenisei, and Lena Rivers. Similar gauging stations were established on the Kolyma, Mackenzie and Yukon between 1968 and 1978 and each continues to generate data. PARTNERS samples were taken at, or as close to these gauging stations as possible. Figure 1 (Chapter 2) shows the six rivers sampled with red dots representing the approximate sampling stations. More specifically, the sampling and gauging stations are listed in Table 2 with exact locations. Sampling was conducted at various times of the year to obtain a representative data set reflecting the changing seasonal hydrograph, including once beneath ice cover. Each river was sampled seven times per year during 2004-2005. The collection device was a torpedo shaped, Teflon coated, 132 lb, depth integrated sampler (US D-96). The rivers were sampled at five different locations along a cross-channel transect and mixed into one homogeneous sample using a Teflon churn. For the winter-time sampling, water was collected through a hole drilled in the ice, making it impossible to sample a cross-channel transect. With the exception of the winter sample, each water sample is representative not only of surface to bottom, but cross-channel chemistry. Water from the Teflon churn was then filtered (0.45 μm Capsule filters) into 1 liter polycarbonate bottles and frozen. All samples remained frozen and in the dark during shipment to MBL and disbursement to project participants.

Table 2. Sampling locations and gauging stations including latitude and longitude coordinates, for rivers investigated in PARTNERS project

	Sampling station	Gauging station
Ob	Salekhard, Russia 66°31'N 66°36'E	Salekhard, Russia 66°31'N 66°36'E
Yenisei	Dudinka, Russia 69°23'N 86° 09'E	Igarka, Russia 67°43'N 86° 48'E
Lena	Zhigansk, Russia 66°46'N 123°22'E	Kyusyur, Russia 70°68'N 127°39'E
Kolyma	Cherskiy, Russia 68°45'N 161°18'E	Kolymskoye, Russia 68°73'N 158°72'E
Yukon	Pilot Station, Alaska 61°56'N 162°52'W	Pilot Station, Alaska 61°56'N 162°52'W
Mackenzie	Tsiigehtchic, Canada 67°26'N 133°45'W	Arctic Red, Canada 67°45'N 133°74'W

Analysis

Various approaches were taken to characterize the composition of DOM. These include the concentration of Dissolved Organic Carbon ([DOC]), optical properties (UV-Vis absorbance and Fluorescence), and lignin phenol analysis.

Dissolved Organic Carbon

The concentration of DOC was determined on a MQ-1001 TOC analyzer following the protocol of Qian and Mopper (1996) with modifications by Peterson et al. (2003). This method employs high temperature combustion of organic carbon, to carbon dioxide with subsequent detection by a non-dispersive infrared detector (LICOR-6252). Samples were acidified (pH 2) with 20% H_3PO_4 to remove inorganic carbon

constituents. Replicate samples were analyzed with three injections per sample. Deep-sea standards (D. Hansell, RSMAS) were used to validate the proper performance of the machine. A calibration curve was created daily with standards bracketing sample concentration. Residual standard deviations were between 2-4% for standards ranging from 200-2000 μM.

Optical Properties

The optical measurements made for this study were UV-Vis absorbance and fluorescence. These types of analysis have the advantage of virtually no sample preparation compared to traditional laboratory techniques while remaining specific enough to describe compositional differences between samples. An additional advantage of using this approach is that DOM remains in a relatively natural state. Optical properties are therefore a cost effective and sensitive approach to describe the bulk chemical composition of DOM.

The basic theory behind optical measurements is that bonding electrons in molecules will become excited after exposure to light following the equation:

$$m + h\upsilon \rightarrow m^*$$

where m is the molecule, hυ is a photon of light and m* is the excited molecule. There are several types of relaxation processes that return the molecule to ground state, and each can be measured using a different instrument. The type of relaxation process the molecule follows typically will minimize the time spent at excited state. Absorbance depends on the transfer of the excess energy in the form of heat (nonradiative), whereas, fluorescence is a reemission of energy in the form of light (Skoog and Leary, 1992).

Absorbance

Absorption of UV-Vis radiation is valuble for identifying functional groups that contain valence electrons with low excitation energies (chromophores) or determining abundance of compounds containing absorbing groups (Skoog and Leary, 1992). The spectra of chromophores tend to be broad because of superposition of vibrational and

electronic transitions of the excited electron. The electronic transitions brought about by organic molecule absorption are dominantly π-π^* and occur most prominently in the UV spectral region, however, some weak absorption does occur in the visable regions. (Skoog and Leary, 1992). The centers specifically termed chromophores have π orbitals provided by a double-bonded, unsaturated functional group. Aromatic structures are conjugated systems and constitute a significant fraction of terrestrial DOM. Conjugation implies a molecular configuration with multiple absorbing centers, resulting in a red shift of absorption primarily in the UV range. With this technique it is not possible to identify specific polymers but an overall reduction in the amount of UV absorbance due to aromatic structures could illustrate a source shift or potentially a higher degradation state of OM.

Various parameters were derived from absorbance scans including the Absorption Coefficient at 375 nm ($a_{\lambda 375}$), Spectral Slope (S), and Specific Absorption Coefficient (SUVA). A previous study (Stedmon et al. 2000) showed that the absorption coefficient at 375 nm ($a_{\lambda 375}$) had a strong correlation with [DOC] making it possible to use this parameter as a proxy for DOC measurements. The spectral slope describes the shape of the curve or the bulk compositional characteristics of the material. Due to its larger molecular weight and greater degree of aromaticity, spectral slopes derived from terrestrial DOM have smaller values than marine DOM (Stabenau and Zika 2004). Generally, a shift from smaller to larger values of S can be observed as DOM becomes more degraded. The SUVA also presents a measure of percent aromaticity of organic matter. Prior studies (Novak et al. 1992; Traina et al. 1990; Weishaar et al. 2003) have shown the absorbance at 254 nm represents the region of π-π^* transitions for arenes and polyenes as determined by C13-NMR. A reduction in the SUVA value would indicate DOM with a lower degree of aromaticity (more oxidized state).

Samples were warmed to room temperature then measured in 5 cm quartz cells on a Shimadzu 2501 spectrophotometer. Scans were made from 200-800 nm with a 1 nm sample interval and 2 nm slit width. Milli-Q water was used as a blank for baseline determination. Data, in the form of absorbance units, was exported to MATLAB to

calculate absorption coefficients (a_λ) (equation 1), S (equation 2) and SUVA (equation 3).

$$a_\lambda = (2.303 * A) / \text{pathlength} \qquad \text{(equation 1)}$$

a_λ=absorption coefficient
A=absorbance (optical density) recorded from spectrophotometer
pathlength=5cm

$$a_\lambda = a_{\lambda 375} * e^{S\,(375-\lambda)} \qquad \text{(equation 2)}$$

a_λ=absorption coefficient
$a_{\lambda 375}$=absorption coefficient at reference wavelength (375nm)
λ=wavelength

$$\text{SUVA}\ (\text{L(mg C)}^{-1}\ \text{m}^{-1}) = A_{\lambda 254} / \text{pathlength} / [\text{DOC}] \qquad \text{(equation 3)}$$

$A_{\lambda 254}$= Absorbance at 254nm
Pathlength=5cm
[DOC]=Dissolved Organic Carbon concentration (mg/L)

The mathematical relationship between the absorption coefficient and wavelength has been modeled by equation 2 (Jerlov 1968, Lundgren 1976, Bricaud et al. 1981), but has been highly controversial and varied in the literature (Twardowski et al 2004). The original method employed log-transformation of the data then application of a linear regression to determine S; however, this results in an underestimated value because weight is placed equally between the UV and visible regions of the spectrum despite the overwhelming amount of absorbance in the UV range. Authors have also used various combinations for reference and scanning wavelengths making it difficult to compare data within the literature. Using equation 2, the non-linear regression technique outlined by Stedmon and Markager (2001) was used on absorption coefficients from 300-650 nm to determine the spectral slope. In this model the reference wavelength and absorption coefficient is set to 375 nm.

Fluorescence

Fluorescence is a unique chemical property of certain molecules. In this process the excited electron is said to be in the singlet state, meaning that the electron in the

higher-energy orbital has the opposite spin as that in the lower-energy orbital (Skoog and Leary, 1992). As described above, the relaxation process results in the emanation of light. By convention we call this emission and the light used to stimulate the process the excitation. Emission is most commonly red-shifted (stokes shift) in liquid samples because of the efficiency of vibrational relaxation (Skoog and Leary, 1992). When the electron returns to ground state it will fall into any one of the vibrational levels. Through collisions of the excited molecules with each other and the solvent, the excess energy will be transferred, resulting in an emission of lower energy (longer wavelength) (Skoog and Leary, 1992). This shift in emission energy is what allows the user to measure fluorescence.

Rayleigh and Raman scattering are a common problem when trying to employ fluorescence spectroscopy because their intensity in most cases is several fold more intense than sample fluorescence. Rayleigh peaks are the result of elastic scatter by small particles. Elastic scatter means there is no change in energy so the peak can be found at the same wavelength as excitation light or twice the excitation wavelength. The rayleigh peak intensity is related to the wavelength of excitation, size of particle, and their polarizability (Skoog and Leary, 1992). The raman effect differs from rayleigh scattering in that a very small part of scattered radiation undergoes frequency changes due to vibrational energy level transitions (Skoog and Leary, 1992). The loss of energy involved in raman scatter will shift this peak to slightly higher wavelengths. The methodology used to remove these scatter effects will be described in detail below.

Several different techniques have been employed to describe the chemical composition of DOM using fluorescence properties. In this study Excitation-Emission Matrices (EEM's) were recorded. EEMs have been used to determine general source characteristics of CDOM (colored dissolved organic matter) typically differentiating between OM described as terrestrial humic, marine humic, and protein-like (Coble et al. 1990, Chen and Bada 1992, Coble 1996, McKnight et al. 2001, and Chen et al. 2004). It has also been used to describe CDOM compositional dynamics as rivers mix with oceans, (Klinkhammer et al. 1997, De Souza Sierra et al 1997, Del Castillo et al. 1999,

Boyd and Osburn, 2004, and Chen and Gardner 2004), as an estimation of DOC concentrations (Laane and Koole, 1982, Ferrari et al. 1996, and Guay et al. 1999) and to track terrestrial DOM distribution in the Nordic Seas (Amon et al. 2003).

Fluorescence measurements were made on filtered river samples in a 1 cm quartz cuvette using a Photon Technologies International fluorometer (Quantum Master-4 SE) with a continuous light source for enhanced sensitivity. EEMs were produced by scanning fluorescence emission (300-600 nm) at a series of excitation wavelengths (240-450 nm) using set slit widths of 5 nm for both excitation and emission. Samples were warmed to room temperature before analysis and milli-Q water was used for blank subtraction. A PTI software (Felix) feature was utilized, which allows the user to correct for instrument biases such as excitation and emission monochromaters as well as light bulb life and efficiency. After data acquisition on the spectrofluorometer the raw data was exported into MATLAB for remaining corrections (inner filtering, scatter removal) and plotting. Fluorescence data was corrected for inner filtering with absorbance data (collected the same day) following the protocol described by McKnight et al. (2001) (equation 4).

$$\text{I.F. Corrected data} = \frac{\text{Raw fluorescence}}{10^{-[(a\lambda ex)(\text{pathlength}) + (a\lambda em)(\text{pathlength})]}} \qquad \text{(equation 4)}$$

Where $a_{\lambda ex}$ and $a_{\lambda em}$ are the absorption coefficients at each excitation-emission wavelength pair, respectively. This removes bias created for concentrated samples where fluorescence might be blocked or absorbed by other fluorophores. Next, the MQ blank was subtracted from the I.F. corrected data to remove Raman scatter and fluorescence created by MQ in regions of interest. Ultimately, this didn't remove the Rayleigh scattering so these regions of the EEM were cut before plotting (see below) as they were several-fold more intense than sample fluorescence. Finally, the intensities were converted into Raman units for inter-lab comparison. The MQ scan was used to

locate and calculate the raman area (Excitation: 350 nm, Emission: 375-421) by integrating the area under the curve. The MQ subtracted-fluorescence intensities were then divided by the raman area to normalize (Raman Units). Plots were also created in MATLAB after regions were cut using a code (flucut.m) created by Colin Stedmon. The code replaced areas affected by scattering peaks with either zero's or NaN's (Not a Number) which MATLAB interprets as "stop plotting." Reference standards (Starna Cells, Inc.) covering the measured range of excitation and emission wavelengths were scanned daily. Comparison of peak size and shape over time allowed for evaluation of the spectrofluorometer's performance.

Lignin Phenols

Vascular plants are made up of 3 major structural chemical components, cellulose, hemi-cellulose, and lignin. Cellulose being the dominant structural component is also more degradable in the environment (Schubert, 1965). Hence, lignin, being resistant to microbial degradation is often used as an indicator of terrestrial DOM in the ocean (Hernes and Benner 2002; Meyersschulte and Hedges 1986; Opsahl and Benner 1997; Opsahl et al. 1999). Lignin does not naturally occur alone in the plant but coexsists with hemi-cellulose (Sarkanen, 1971). The function of this macromolecule is rigidity, defense against fungal attack, and transport of nutrients, water, and metabolites (Sarkanen, 1971). The actual form of lignin is relatively unclear because the strength of the macromolecule requires severe chemical conditions for breakdown. Various analytical methods have been used and all derive different results; however, all can agree that lignin is composed of phenylpropane building units joined together by carbon-carbon bonds and ethereal linkages (Schubert, 1965). The three main components are trans-coniferyl, trans-sinapyl, and trans-p-coumaryl alcohols (Sarkanen, 1971). Due to the destructive nature of these methods the "lignin" that is analyzed is termed lignin oxidation products (LOP) because they are not found naturally in vascular plants. Using various proportions of these products lignin source (angiosperm, gymnosperm, herbaceous, woody, and non-woody) and its degradation state (microbial or photo-

oxidative) can be described. These ratios can also be used as indicators of process oriented controls on lignin composition such as leaching and sorption/desorption.

Lignin for this study was analyzed using alkaline hydrolysis. The established protocol was described by Hedges and Ertel (1982) with modifications by Goni and Hedges (1992), Goni and Montgomery (2000) and Louchouarn et al. (2000). A portion (~ 1 L) of the filtered water sample was acidified (pH 2) and subjected to Solid Phase Extraction (SPE), which involves sorption of DOM to a solid phase within a column. Briefly, columns were purchased (Varian) pre-packed with 10g of octadecyl carbon moieties (C_{18}) bonded to a silica support. The columns were prepared by rinsing with 50 ml methanol then 100 ml acidified (pH 2) Milli-Q water. A volume of sample was washed over the column at a flow rate of 100mL min^{-1} to maximize extraction efficiency. The column was subsequently washed with 0.5 L of acidified (pH 2) Milli-Q water to remove salts. Hydrophobic material was removed from the column by elution with 50mL methanol and dried in a Savant Speed Vacuum (210A).

The proportion of lignin oxidation products quantified (see below) can reflect the isolation efficiency of the column. Quantitative and qualitative efficiencies of the column are influenced by the concentration of organic material and its composition (Louchouarn et al., 2000). Early work (Mills et al. 1982) using unacidified estuarine samples and smaller columns (500mg of solid phase) showed 38% of total DOC was extracted, quantitatively. In contrast, Louchouarn et al. (2000) suggested that efficiency was controlled by the relative amount of lignin not purely the sample carbon concentration. Another study conducted on river water found that over 60% of the original DOM was extracted using C_{18} solid phase extraction disks (Kim et al. 2003). An additional concern is the occurrence of selective sorption influenced by chemical properties of some oxidation products relative to others. Louchouarn et al. (2000) showed there was some selective sorption of acid and aldehyde oxidative products when column loading was at both the high and low ends (carbon retained); therefore sample volumes of 2-4 L (4-10 mg DOC L^{-1}) were recommended to insure proper column loading for river samples. Arctic Rivers generally have higher concentrations of lignin

relative to carbon than those used in the Louchouarn et al. (2000) study so for some samples smaller volumes were extracted; however, the $(ad/al)_v$ were interpreted with caution for the samples nearing the lower or higher ends of Louchouarn's suggested volumes.

Dried extracts were resuspended in 2 N NaOH and oxidized at 155ºC with CuO and $Fe(NH_4)(SO_4)_2 \cdot 6H_2O$ in the absence of oxygen. The oven was temperature controlled to ramp to 155ºC at a rate of 4ºC min^{-1} and hold for 150 minutes while the bombs were constantly rotated insuring contact of sample and CuO. Bombs were removed from the oven and LOP were separated from CuO in a centrifuge using 1 N NaOH. After separation, LOP were extracted using ethyl acetate. Residual water was removed from ethyl acetate with anhydrous Na_2SO_4 before samples were dried for subsequent analysis on a Thermo Finnegan Trace Gas Chromatograph coupled to a Polaris Q Mass Spectrometer (GC/MS). Dried samples were redissolved in pyridine and derivatized with regisil for one hour at 78ºC prior to GC/MS injection. The samples were injected into a splitless liner containing glass wool to improve the rate of vaporization. Helium gas (1.3 ml/min) carried the sample into the column (DB-5MS, 30 m, 0.25 mm i.d.; J&W Sic, no. 122-5532). The GC oven was programmed to ramp from 100ºC to 300ºC at a rate of 4ºC min^{-1} then to hold for 16 minutes. The injection port was set to 300ºC, the GC/MS transfer interface to 280ºC, and the MS source to 300ºC.

Trimethylsilyl derivatives were detected in full scan mode (50-400 m/z) using 3-5 ions for identification of each LOP, but one for quantification (Table 3). Ethyl Vanillin (EVAL) and Cinnamic Acid (CiAD) were added to each sample as an internal/recovery standard. CiAD was used for calculation of response factors and LOP concentration. The ratio of EVAL/CiAD served as a quality control due to the sensitivity of aldehydes to degradation or vaporization compared to acids.

Table 3. Retention times (RT; min) and ions used to identify lignin oxidation products. The ion in italics was used for quantification. LOP grouped into vanillyl, syringyl, cinnamyl, and p-hydroxy.

GROUP	LOP NAME	RT	IONS
V	Vanillin (VAL)	14.18	*194*, 209, 224
	Acetovanillone (VON)	16.42	*193*, 208, 223, 238
	Vanillic Acid (VAD)	20.18	*297*, 298, 312, 313
S	Syringealdehyde (SAL)	18.56	*239*, 224
	Acetosyringone (SON)	20.22	*238*, 253, 268
	Syringic Acid (SAD)	23.78	*253*, 297, 327, 312
C	*p*-Coumaric Acid (CAD)	24.73	*249*, 293, 219, 308
	Ferulic Acid (FAD)	28.30	*308*, 338, 323
P	*p*-Hydroxybenzaldehyde (PAL)	9.88	*179*, 194, 239
	p-Hydroxyacetophenone (PON)	12.41	*193*, 208
	p-Hydroxybenzoic Acid (PAD)	16.69	*267*, 161, 220
	3,5 Dihydroxybenzoic Acid (DiBA)	21.86	*370*

Reproducibility and linearity of method were tested using a NIST sediment standard (1944 New York-New Jersey Waterway Sediment). Replicate oxidations of sediment yielded residual standard deviations of total V, S, C, and P ranging from 6.1-7.2%. Total lignin normalized to dry sediment weight (75-175 mg) also proved to be linear (R^2=0.97; data not shown). Inter-lab comparison of total LOP yields and proportions showed oxidation and GC/MS conditions were similar. Reagent blanks and sediment standards were processed daily as additional quality control measures. Some contamination was found in the reagent blanks, however, it was always minimal therefore no blank subtraction on done. Analysis of SPE blanks found only trace contamination of the acidic groups (Vanillic Acid, Syringic Acid, *p*-Hydroxybenzoic Acid, 3,5 Dihydroxybenzoic Acid).

Low Carbon Samples

Samples with a low carbon concentration were amended with glucose (10 mg) prior to oxidation in order to prevent superoxidation, which would result in elevated $(ad/al)_v$ ratios. In several (n=9) of these samples lignin yields were low (0.04-0.15 mg LOP/100 mg OC) enough that certain oxidation products, mostly in the syringyl group, were below the level of detection of the Polaris Q. These samples were re-run on a Varian 3800/4000 GC/MS system using a Varian Factor 4, 0.25 ID and 60 m column which had higher sensitivity compared to the Polaris Q. A NIST sediment sample that had been previously measured on the Polaris Q was run on the Varian for instrument comparison. Lignin yields of this standard were 16% higher on the Varian than the Polaris Q which were comparable to the daily variation of all sediment standards (n=8) measured on the Polaris Q (18.7%) (table 4). Ratios were also within the daily variation for sediment standards (table 4); however, these data were interpreted cautiously.

Table 4. Lignin parameter data from one NIST sediment standard generated using the Thermo Finnegan Trace GC-Polaris Q mass spectrometer and the Varian 3800/4000 GC/MS. (Σ8= Sum of LOP μg/L, Λ8=mg LOP/100 mg OC, S/V=syringyls/vanillyls, C/V=cinnamyls /vanillyls, $(ad/al)_v$ = the ratio of vanillic acid to acetovanillone, DiBA/V=3,5 Dihydroxybenzoic acid/vanillyls, P/(P+S)= total *p*-hydroxy group/(*p*-hydroxy group+Syringyl), PON/P =*p*-Hydroxyacetophenone/ total *p*-hydroxy group, CAD/FAD=*p*-coumaric acid/ferulic acid)

	Σ8	Λ8	S/V	C/V	$(ad/al)_v$	DiBA/V	P/(P+S)	PON/P	CAD/FAD
Polaris Q	0.55	1.25	0.67	0.17	0.25	0.04	0.12	0.13	1.39
Varian	0.65	1.49	0.66	0.22	0.30	0.06	0.16	0.19	1.47
%Diff *	16	16	-2	22	19	38	25	29	6
RSD $^{\Psi}$	19	19	14	22	17	35	20	55	30

* % Diff indicates the percent difference between the two instruments with the Varian detecting more LOP than the Polaris Q.
$^{\Psi}$ RSD (n=8) is the residual standard deviation of all the sediments standards measured on the Polaris Q.

CHAPTER IV

RESULTS

Yukon River

Dissolved Organic Carbon (DOC)

DOC follows the typical pattern for Arctic Rivers with highest concentrations (~17.5-20 mg L^{-1}) at peak river discharge in May and June, and rapidly declining values during July and August to base flow concentrations of ~2.5 mg L^{-1} from September to April (Figure 2a; Table 5). The discharge weighted annual average DOC concentration in the Yukon was 6.01 mg L^{-1} in 2004 and 8.95 mg L^{-1} in 2005 (Table 6). Based on the monthly means for discharge and DOC concentrations the total annual discharge of DOC by the Yukon is estimated at 1.11 Tg for 2004 and 2.74 Tg for 2005 (Table 6). In 2005, the area weighted annual discharge was almost 3x larger (3223 kg C $km^{-2}yr^{-1}$) than in 2004 (1305 kg C km^{-2} yr^{-1}) and was close to the largest estimates reported in this study from the Lena River (Table 6). It is interesting to note that the DOC concentration in the Yukon drops much faster than does the discharge (Figure 2a, Table 5).

Optical Properties

The absorption coefficient at 375 nm (a_{375}) also followed the discharge rather well with the highest values occurring at peak flow and lowest at base flow (Figure 2b). Generally, the absorption coefficient at 375 nm was strongly correlated with DOC (r^2 =0.86; data not shown). Specific UV absorption at 254 nm (SUVA) which indicates the relative abundance of aromatics was lowest at base flow (1.6-1.9 $L(mg\ C)^{-1}$ m^{-1}), and larger at peak discharge (2.2-2.7 $L(mg\ C)^{-1}$ m^{-1}) (Figure 2c). In 2004 the trend is clearly visible, however, in 2005 the data are more scattered (Figure 2c). SUVA's generally compare well with the other rivers. In the spring SUVA's from the Yukon are slightly smaller than those measured for the Ob, Lena, and Yenisei but are consistent across

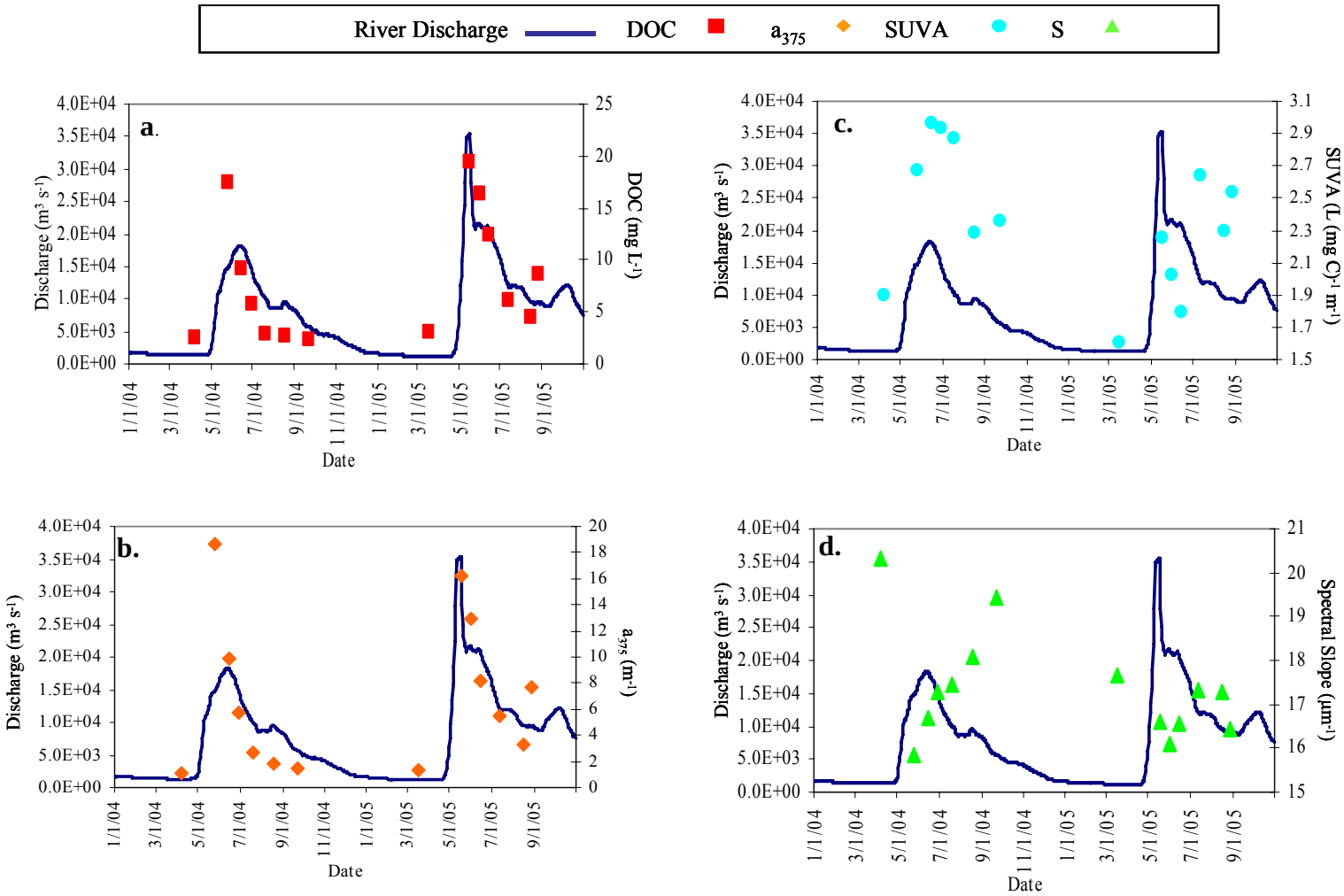

Figure 2. Yukon River discharge ($m^3\ s^{-1}$), and a) Dissolved organic carbon (DOC; mg L^{-1}), b) Absorption coefficient at 375 nm (a_{375}; m^{-1}), c) Specific ultraviolet absorption coefficient (SUVA; L(mg OC)$^{-1}$ m^{-1}) and d) Spectral slope (S; μm^{-1}) for the years 2004 and 2005.

Table 5. Seasonal data from all rivers including sample date, discharge, DOC, S, SUVA, a_{375}. Discharge data for the Yukon was generated by USGS, Mackenzie by Water Survey of Canada, and the Ob, Yenisei, Lena and Kolyma by The State Hydrological Institute in St. Petersburg, Russia.

River	*Sample date*	*Discharge*	*DOC*	*S*	*SUVA*	a_{375}
		$m^3\ s^{-1}$	$mg\ L^{-1}$	μm^{-1}	$L\ (mg\ C)^{-1}\ m^{-1}$	m^{-1}
Yukon	4/3/04	1317	2.5	20.3	1.9	1.1
Yukon	5/26/04	14838	17.4	15.9	2.7	18.7
Yukon	6/15/04	18094	9.1	16.7	2.9	9.9
Yukon	6/29/04	14555	5.8	17.3	2.9	5.8
Yukon	7/19/04	10052	2.9	17.44	2.9	2.7
Yukon	8/18/04	9458	2.7	18.1	2.3	1.9
Yukon	9/22/04	5720	2.4	19.4	2.4	1.5
Yukon	3/17/05	1245	3.0	17.7	1.6	1.3
Yukon	5/17/05	35400	19.4	16.6	2.3	16.3
Yukon	6/1/05	21480	16.4	16.1	2.0	12.9
Yukon	6/14/05	20940	12.4	16.6	2.7	8.2
Yukon	7/12/05	12240	6.2	17.3	2.6	5.4
Yukon	8/16/05	9510	4.5	17.3	2.3	3.3
Yukon	8/27/05	9390	8.6	16.4	2.5	7.7
Mackenzie	3/24/04	3780	4.0	21.5	1.6	1.2
Mackenzie	6/17/04	18300	4.9	16.7	2.5	4.1
Mackenzie	6/22/04	17400	4.3	19.4	2.4	2.8
Mackenzie	7/13/04	12500	3.8	21.2	2.1	1.7
Mackenzie	8/4/04	12400	3.7	19.1	1.9	1.8
Mackenzie	8/25/04	8730	3.4	22.9	1.9	1.2
Mackenzie	9/8/04	8770	3.0	21.5	1.9	1.1
Mackenzie	3/16/05	3670	3.3	21.5	2.0	1.3
Mackenzie	6/14/05	25200	5.5	17.4	2.5	4.4
Mackenzie	6/29/05	16900	5.7	17.7	2.2	3.9
Mackenzie	7/14/05	16200	5.4	18.0	2.3	3.6
Mackenzie	8/9/05	13500	4.4	18.6	2.5	3.0
Mackenzie	8/30/05	12300	4.9	18.9	2.2	3.0
Mackenzie	9/13/05	12200	4.7	18.8	2.2	2.8

Table 5. Continued

River	*Sample date*	*Discharge*	*DOC*	*S*	*SUVA*	a_{375}
		$m^3 s^{-1}$	$mg L^{-1}$	μm^{-1}	$L (mg C)^{-1} m^{-1}$	m^{-1}
Lena	4/9/04	2275	6.6	16.0	2.9	7.6
Lena	6/5/04	61408	17.2	16.2	3.6	23.6
Lena	6/7/04	90720	18.2	15.6	3.7	26.4
Lena	8/19/04	35500	7.8	15.9	2.8	8.6
Lena	8/24/04	31100	7.3	17.0	2.8	7.1
Lena	10/7/04	24800	7.0	16.7	2.8	7.3
Lena	10/10/04	26189	8.5	16.1	2.9	9.7
Lena	3/24/05	3947	9.9	17.2	2.8	9.5
Lena	5/27/05	53784	19.2	16.2	2.9	21.7
Lena	6/4/05	109800	17.5	14.9	2.9	22.4
Lena	8/6/05	45500	13.3	15.8	2.2	11.6
Lena	8/14/05	37700	10.8	16.0	2.4	10.1
Lena	10/9/05	23900	8.3	16.5	2.6	8.1
Lena	10/10/05	23200	7.6	16.8	2.7	7.5
Kolyma	6/11/04	17300	12.3	15.7	2.9	14.5
Kolyma	6/15/04	15020	11.0	17.0	2.7	10.8
Kolyma	6/25/04	11700	7.2	16.5	2.5	6.7
Kolyma	7/15/04	7140	6.7	16.8	2.5	6.1
Kolyma	8/10/04	4810	4.7	17.1	2.2	3.6
Kolyma	9/23/04	3000	4.8	17.6	2.2	3.5
Kolyma	4/22/05	ND	3.0	17.6	2.7	2.7
Kolyma	6/30/05	ND	6.0	17.9	2.2	4.1
Kolyma	7/19/05	ND	5.6	17.2	2.2	4.1
Kolyma	8/14/05	ND	6.2	17.7	2.7	5.4
Kolyma	8/27/05	ND	11.3	16.6	2.2	9.4
Kolyma	8/27/05	ND	11.3	16.6	2.2	9.4
Kolyma	9/12/05	ND	6.4	17.6	2.4	5.0
Kolyma	9/29/05	ND	7.4	17.6	2.2	5.4

Table 5. Continued

River	*Sample date*	*Discharge*	*DOC*	*S*	*SUVA*	a_{375}
		$m^3 s^{-1}$	$mg L^{-1}$	μm^{-1}	$L (mg C)^{-1} m^{-1}$	m^{-1}
Ob	4/5/04	3692	4.5	18.6	2.2	2.9
Ob	6/15/04	34500	8.6	16.2	3.4	11.3
Ob	6/17/04	34500	10.3	16.6	2.9	11.3
Ob	7/28/04	26000	12.1	16.3	3.1	13.7
Ob	8/11/04	15900	12.3	17.1	2.6	11.0
Ob	10/11/04	8920	9.6	19.0	2.3	6.4
Ob	10/14/04	9600	9.4	17.6	2.6	8.2
Ob	3/15/05	4049	8.5	18.7	1.9	4.8
Ob	6/4/05	34800	11.2	15.9	2.9	13.1
Ob	6/6/05	34800	12.7	15.6	2.7	14.0
Ob	6/28/05	29200	11.4	16.4	3.3	14.2
Ob	7/14/05	26600	12.7	16.7	3.1	14.6
Ob	9/5/05	9760	12.4	17.3	2.7	11.3
Ob	9/17/05	8890	11.3	17.1	2.8	10.8
Yenisei	3/19/06	7500	2.5	18.8	2.2	1.5
Yenisei	6/14/04	98500	15.0	15.5	3.5	22.4
Yenisei	6/16/04	94500	14.3	15.9	3.7	21.3
Yenisei	6/18/04	90600	13.3	15.7	3.5	19.6
Yenisei	8/25/04	18200	5.7	17.5	2.3	4.2
Yenisei	10/1/04	19880	7.8	16.2	2.7	8.3
Yenisei	10/2/04	19370	8.2	16.2	2.7	8.8
Yenisei	3/26/05	12850	3.0	17.2	1.4	1.4
Yenisei	6/11/05	78800	12.3	15.3	3.2	17.5
Yenisei	6/16/05	54900	11.8	15.4	3.1	15.8
Yenisei	6/17/05	51500	13.1	15.8	2.7	14.8
Yenisei	8/16/05	14290	8.3	17.1	1.9	5.4
Yenisei	8/21/05	14150	6.1	17.7	2.8	5.4
Yenisei	9/21/05	15310	5.2	17.2	2.9	5.3

Table 6. Estimated annual dissolved organic carbon (DOC) export for 2004 and 2005. DOC is presented as the discharge weighted annual mean DOC concentration (mg L^{-1}), the annual estimated DOC export (Tg yr^{-1}) as well as the area weighted DOC export (kg DOC km^{-2} yr^{-1}.

River	Year	Discharge Weighted mean DOC	Annual Estimated DOC export	Area weighted DOC export
		mg L^{-1}	Tg yr^{-1}	kg DOC km^{-2} yr^{-1}
Yukon	2004	6.01	1.11	1305
Yukon	2005*	8.95	2.74	3223
Mackenzie	2004	3.77	0.95	555
Mackenzie	2005*	4.79	1.69	988
Ob	2004	9.33	3.24	1260
Ob	2005*	11.15	3.99	1552
Yenisei	2004	9.50	6.12	2372
Yenisei	2005*	7.26	4.47	1732
Lena	2004	11.94	6.78	2801
Lena	2005*	13.46	8.93	3690
Kolyma$^{\Psi}$	2004	7.32	0.72	1074
Kolyma$^{\Psi}$	2005*	8.13	0.88	1313

*An estimate was made for November and December 2005 discharge based on data from 2004 and October of 2005.

$^{\Psi}$ Discharge from November and December of 2004 was estimated based on January and October of 2004. Discharge data from 2005 was not available so 2004 data was used.

rivers during the winter. Spectral slopes decrease from the maximal value of 20.3 μm^{-1} in spring of 2004 to the lowest values during freshet 15.8 μm^{-1} and gradually rise again as the river returns to base flow (Figure 2d). In 2005 the spread between base flow and peak flow (17.7 to 16.6 μm^{-1}) was not as great but the same trend as 2004 was visible (Figure 2d). S values from the Yukon are consistent with other rivers in the spring whereas in the winter values from the Yukon and Mackenzie are somewhat larger than Eurasian rivers. It seems that qualitative measures like spectral slope and SUVA are not as strongly related to discharge as DOC and respond to changes in discharge somewhat slower than DOC concentration (Figure 3) which is somewhat unique to the Yukon. Overall, fluorescence intensities where also highest during May (Figure 4bd) and lowest in March (Figure 4ac) in both years. Peaks of highest fluorescence intensity where associated with the following wavelengths pairs, Ex: 240, Em:425-475 and Ex:315, Em:400-475 (Figure 5abcd). Locations of fluorescence maxima did not change seasonally but the intensity increases about 10-fold between base and peak flow samples (Figure 5abcd). Seasonal differences of fluorescence peak intensities indicate the large fluctuations between peak flow and base flow conditions (Figure 5). In 2005, the last sample of the year (September) had enhanced fluorescence relative to summer samples (Figure 5cd) which is consistent with increases in DOC, and SUVA, and decreases in spectral slopes, as well as increases in lignin yields (see below). Maximum seasonal fluorescence intensities were similar to the Ob and Kolyma, whereas minimum fluorescence was more comparable to the Mackenzie and Yenisei.

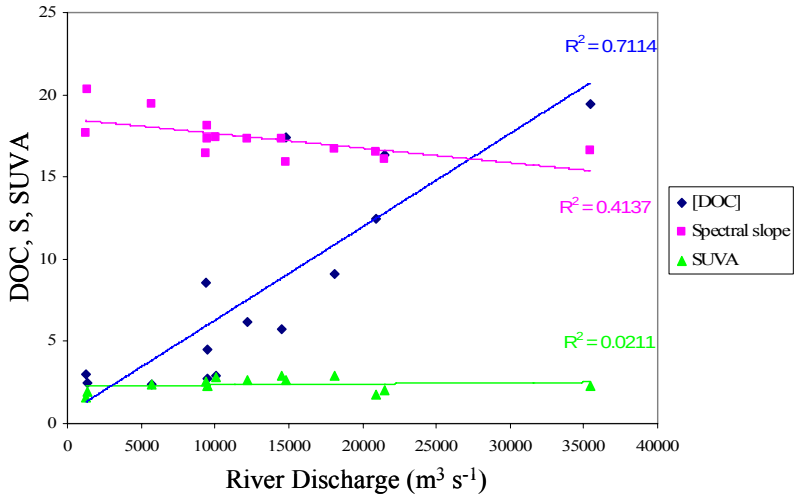

Figure 3. Relationship of Yukon discharge to DOC (mg L^{-1}), spectral slope (μm^{-1}), and SUVA (L (mg OC)$^{-1}$ m^{-1}).

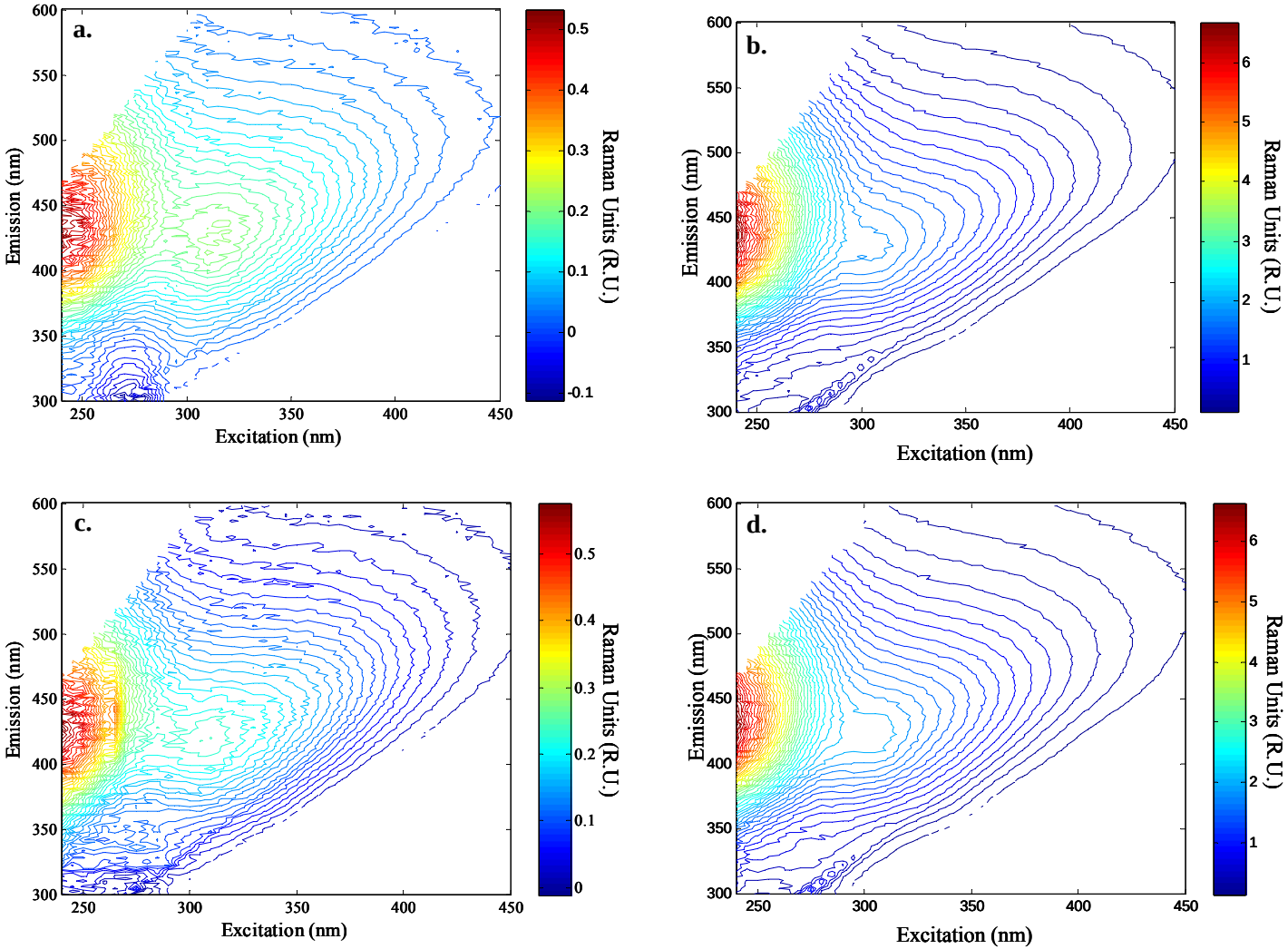

Figure 4. Fluorescence EEM's measured in Yukon samples from low flow (a,c) and peak flow (b,d) conditions in 2004 (upper panals) and 2005 (lower panals). Note each subplot is on a different scale.

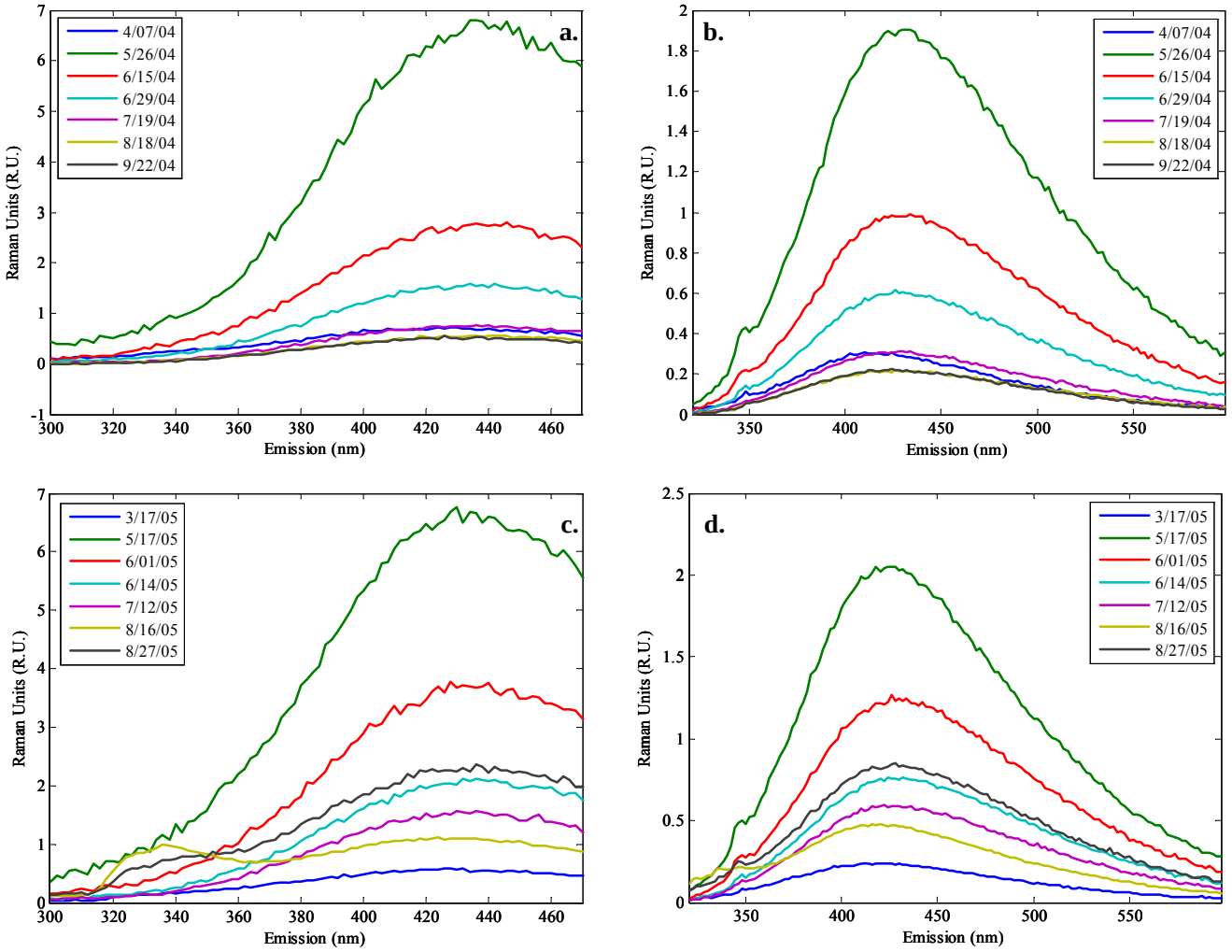

Figure 5. Seasonal variation in the maximum fluorescence intensity measured at excitation 240 nm (a & c) and 315 nm (b & d) for the Yukon River in 2004 (a & b) and 2005 (c & d).

Lignin Phenols

The lignin phenol concentration (Σ8) changed dramatically between base flow (3.29-4.27 μg L^{-1}) and peak flow (97.10-100.99 μg L^{-1}) in both years (Table 7). After peak-flow the concentration of lignin dropped by more than 50% within a few weeks (Figure 6a). Lignin concentrations from the Yukon were comparable to the Kolyma but much larger than the Mackenzie and Ob. The carbon normalized lignin yield (Λ8) showed that lignin contributed approximately three times more organic carbon at peak discharge in both 2004 and 2005 (Λ8=0.39-0.45 mg $(100mg\ OC)^{-1}$) than at base flow (Λ8=0.10-0.12 mg$(100mg\ OC)^{-1}$) (Figure 6b; Table 7). Λ8 from the Yukon was similar to the Ob, and much less than from the Kolyma, Lena, and Yenisei. Lignin ratios showed interesting seasonal differences in DOM quality in both 2004 and 2005. At base flow the ratio of the acid to aldehyde from the vanillyls ((ad/al)v) are low (0.93, 0.57, for 2004 and 2005 respectively) increasing to their maximal values (1.67, 1.85 for 2004 and 2005 respectively) at peak discharge then decrease again as the river returns to base flow (Figure 6c). These values are consistent with the Eurasian rivers. Acid/aldehyde ratios of the syringyls follow a similar pattern in 2004 and 2005, despite some minor scattering later in 2004 (Figure 6c). Syringyl/vanillyl (S/V) ratios for the Yukon don't show any apparent seasonal trend (Figure 6d). In 2004 S/V ratios decrease from base flow to peak flow and continue to decrease as the river returns to base flow. In 2005 the values are more scattered with a mean of 0.52 ± 0.05 (SD) (Figure 6d.). This pattern is fairly consistent across rivers. The cinnamyl/vanillyl (C/V) ratios show an interesting reduction from base flow to peak flow in both 2004 and 2005 (Figure 6d), which is unique to the Yukon. The ratio of 3,5 Dihydroxybenzoic acid to the sum of vanillyls (DiBA/V) and the ratio of total p-hydroxy groups to vanillyls and syringyls (P/(V+S)) both drop at peak discharge from the largest values which occurred during base flow (Figure 6e) similar to other rivers. P-coumaric acid to ferulic acid (CAD/FAD) shows the same trend in 2004 as 2005, the ratios drop dramatically from base flow (4.77, 3.70 for 2004, 2005 respectively) to peak flow (0.43,0.41 for 2004, 2005 respectively) then increase again as the river returns to base flow (Figure 6f) while p-

hydroxyacetophenone/p-hydroxy group (PON/P) remained constant. The CAD/FAD and PON/P trends are common across watersheds.

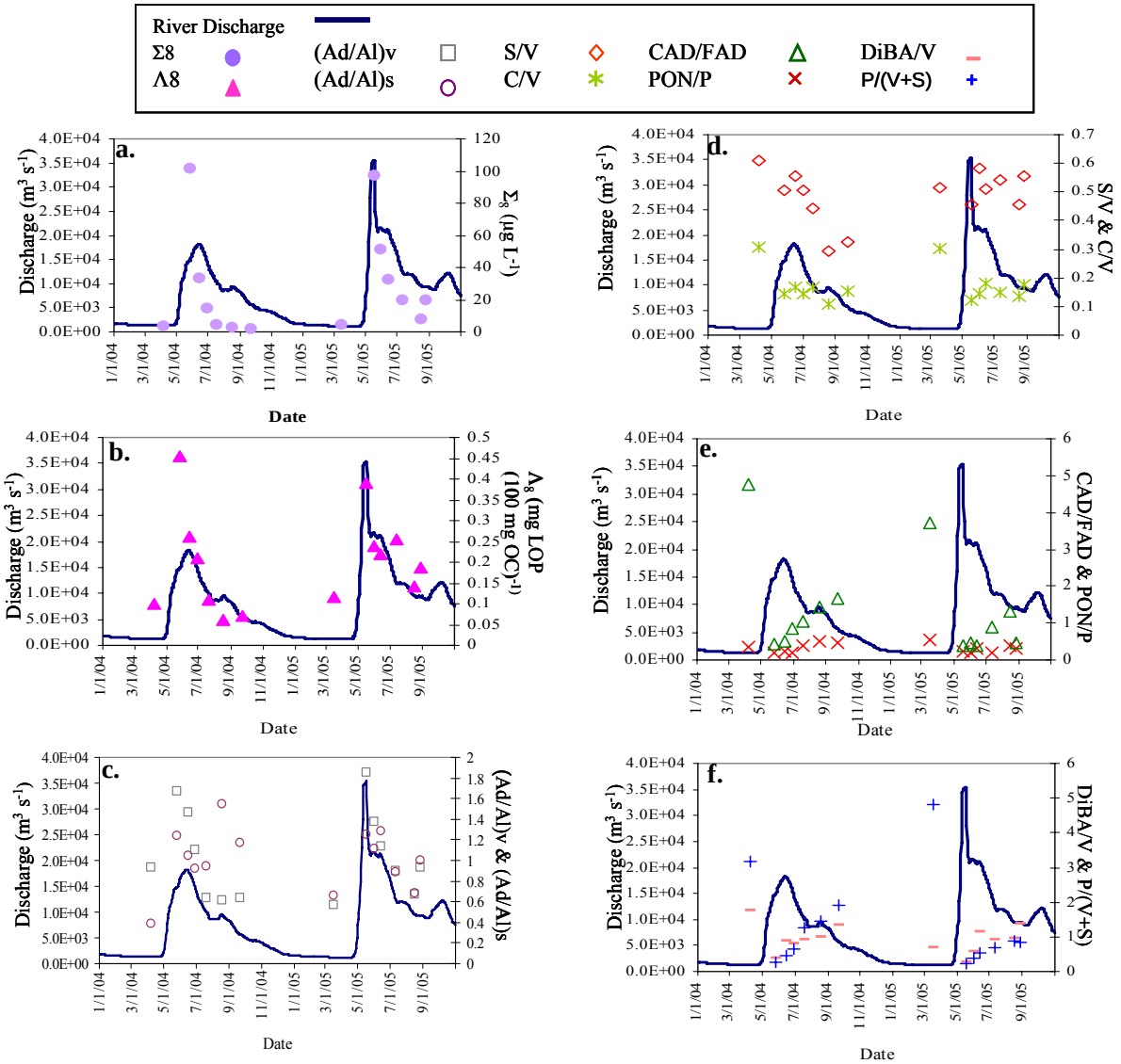

Figure 6. Yukon River discharge and a) Sigma 8 (Σ_8; µg/L), b) Lambda 8 (Λ_8; mg LOP/ 100 mg OC), c) Acid to aldehyde ratios for vanillyls and syringyls, d) Syringyls/Vanillyls (S/V) & Cinnamyls/ vanillyls (C/V), e) p-coumaric acid/ferulic acid (CAD/FAD) & p-hydroxybenzaldehyde/total p-hydroxy group (PON/P), f) 3,5-dihydroxybenzoic acid/vanillyl (DiBA/V) & total p-hydroxy group/(vanillyl + syringyl) (P/(V+S))

Table 7. Seasonal data from all rivers including sample date, discharge, Σ8, Λ8, S/V, C/V, $(ad/al)_v$, DiBA/V, P/(V+S), PON/P, CAD/FAD. Discharge data for the Yukon was generated by USGS, Mackenzie by Water Survey of Canada, and the Ob, Yenisei, Lena and Kolyma by The State Hydrological Institute in St. Petersburg, Russia.

River	Sample date	Discharge	Σ8	Λ8	S/V	C/V	$(ad/al)_v$	DiBA/V	P/(V+S)	PON/P	C/F
		$m^3 s^{-1}$	$\mu g L^{-1}$	mg LOP (100 mg OC)$^{-1}$							
Yukon*	4/3/04	1317	3.3	0.10	0.61	0.31	0.93	1.77	3.19	0.36	4.77
Yukon	5/26/04	14838	101.0	0.45	0.50	0.14	1.67	0.38	0.26	0.21	0.43
Yukon	6/15/04	18094	33.2	0.26	0.55	0.17	1.47	0.88	0.44	0.22	0.50
Yukon	6/29/04	14555	14.7	0.21	0.51	0.14	1.10	0.79	0.63	0.18	0.85
Yukon	7/19/04	10052	4.0	0.11	0.44	0.17	0.64	0.93	1.24	0.40	1.05
Yukon	8/18/04	9458	2.2	0.06	0.29	0.11	0.62	0.98	1.45	0.50	1.43
Yukon	9/22/04	5720	2.0	0.07	0.32	0.15	0.63	1.35	1.92	0.45	1.66
Yukon*	3/17/05	1245	4.3	0.12	0.51	0.30	0.57	0.70	4.82	0.55	3.7
Yukon	5/17/05	35400	97.1	0.39	0.46	0.12	1.85	0.28	0.25	0.22	0.41
Yukon	6/1/05	21480	51.3	0.24	0.58	0.15	1.37	0.57	0.37	0.21	0.46
Yukon	6/14/05	20940	32.6	0.22	0.51	0.18	1.13	1.13	0.53	0.30	0.39
Yukon	7/12/05	12240	19.3	0.25	0.54	0.15	0.90	0.90	0.69	0.20	0.90
Yukon*	8/16/05	9510	8.0	0.14	0.46	0.14	0.67	0.94	0.89	0.39	1.33
Yukon	8/27/05	9390	19.9	0.19	0.55	0.18	0.93	1.38	0.85	0.32	0.47
Mackenzie	3/24/04	3780	2.7	0.06	0.17	0.11	0.96	0.80	0.69	0.18	1.08
Mackenzie	6/17/04	18300	7.4	0.12	0.29	0.11	1.16	0.82	0.68	0.27	0.74
Mackenzie	6/22/04	17400	11.9	0.24	0.22	0.11	0.91	0.41	0.26	0.29	0.54
Mackenzie	7/13/04	12500	4.1	0.08	0.31	0.10	1.10	0.82	0.70	0.19	1.25
Mackenzie	8/4/04	12400	3.9	0.08	0.19	0.13	0.87	0.59	0.35	0.32	0.52
Mackenzie	8/25/04	8730	2.7	0.07	0.19	0.13	0.90	0.65	0.46	0.34	1.06
Mackenzie*	9/8/04	8770	4.9	0.15	0.30	0.12	0.75	0.87	1.96	0.60	1.30
Mackenzie*	3/16/05	3670	4.9	0.11	0.31	0.11	0.75	0.95	2.32	0.61	1.16
Mackenzie	6/14/05	25200	10.1	0.16	0.36	0.09	1.16	0.70	0.54	0.28	1.06
Mackenzie	6/29/05	16900	7.9	0.13	0.30	0.10	1.08	0.73	0.57	0.20	0.74
Mackenzie	7/14/05	16200	6.4	0.11	0.41	0.13	1.04	0.84	0.70	0.26	0.72
Mackenzie	8/9/05	13500	9.2	0.19	0.20	0.12	0.78	0.45	0.30	0.33	0.58
Mackenzie	8/30/05	12300	5.4	0.10	0.25	0.12	1.14	0.88	0.86	0.31	0.69
Mackenzie*	9/13/05	12200	1.9	0.04	0.40	0.15	0.85	0.61	0.89	0.63	0.63

*Samples were measured on Varian

Table 7. Continued

River	*Sample date*	*Discharge*	*Σ8*	*Λ8*	*S/V*	*C/V*	*$(ad/al)_v$*	*DiBA/V*	*P/(V+S)*	*PON/P*	*C/F*
		$m^3 s^{-1}$	$\mu g L^{-1}$	mg LOP (100 mg OC)$^{-1}$							
Ob	4/5/04	3692	6.1	0.12	0.29	0.22	0.56	0.63	3.94	0.60	5.41
Ob	6/15/04	34500	47.6	0.46	0.40	0.11	1.48	0.39	0.48	0.43	0.75
Ob	6/17/04	34500	48.2	0.41	0.58	0.16	1.58	0.61	0.67	0.44	0.81
Ob	7/28/04	26000	41.4	0.30	0.97	0.32	1.43	1.36	0.95	0.26	0.52
Ob	8/11/04	15900	30.0	0.22	1.29	0.36	1.11	1.13	0.81	0.30	1.05
Ob	10/11/04	8920	23.3	0.15	0.34	0.13	1.35	0.72	1.38	0.51	1.46
Ob	10/14/04	9600	17.6	0.16	0.56	0.21	1.23	1.19	1.88	0.49	1.52
Ob	3/15/05	4049	6.0	0.06	0.51	0.11	0.67	0.60	1.03	0.33	1.37
Ob	6/4/05	34800	60.1	0.45	0.64	0.25	1.56	0.80	0.51	0.30	0.49
Ob	6/6/05	34800	62.7	0.46	0.52	0.16	1.47	0.59	0.64	0.23	0.72
Ob	6/28/05	29200	42.3	0.35	0.63	0.21	1.05	0.65	0.69	0.29	0.61
Ob	7/14/05	26600	32.7	0.23	0.75	0.24	1.05	0.91	0.85	0.27	0.68
Ob	9/5/05	9760	17.4	0.12	0.57	0.19	1.27	1.41	1.32	0.30	0.88
Ob	9/17/05	8890	16.6	0.13	0.60	0.20	1.20	1.49	1.45	0.32	1.02
Yenisei	3/19/06	7500	4.0	0.14	0.16	0.08	0.56	0.40	0.65	0.43	0.72
Yenisei	6/14/04	98500	141.8	0.84	0.30	0.09	1.60	0.22	0.20	0.25	0.35
Yenisei	6/16/04	94500	144.3	0.85	0.30	0.08	1.69	0.25	0.19	0.20	0.34
Yenisei	6/18/04	90600	107.7	0.81	0.32	0.08	1.75	0.26	0.22	0.14	0.44
Yenisei	8/25/04	18200	9.2	0.14	0.24	0.09	1.05	0.67	0.54	0.16	0.74
Yenisei	10/1/04	19880	28.4	0.30	0.32	0.09	0.93	0.50	0.46	0.29	0.74
Yenisei	10/2/04	19370	36.3	0.38	0.33	0.09	0.87	0.48	0.38	0.32	0.79
Yenisei*	3/26/05	12850	20.6	0.53	0.32	0.10	0.75	0.21	1.16	0.53	1.19
Yenisei	6/11/05	78800	138.5	0.97	0.55	0.06	1.24	0.35	0.15	0.27	1.05
Yenisei	6/16/05	54900	105.7	0.83	0.29	0.09	1.19	0.34	0.20	0.23	0.30
Yenisei	6/17/05	51500	52.8	0.39	0.34	0.08	1.56	0.33	0.26	0.21	0.44
Yenisei	8/16/05	14290	12.7	0.15	0.29	0.14	1.62	0.78	0.50	0.20	0.25
Yenisei	8/21/05	14150	14.1	0.22	0.24	0.09	1.09	0.69	0.53	0.14	0.69
Yenisei	9/21/05	15310	13.2	0.23	0.27	0.08	1.02	0.50	0.48	0.23	0.57

Table 7. Continued

River	Sample date	Discharge	Σ8	Λ8	S/V	C/V	$(ad/al)_v$	DiBA/ V	P/ (V+S)	PON/ P	C/F
		$m^3 s^{-1}$	$\mu g L^{-1}$	mg LOP (100 mg OC)$^{-1}$							
Lena	4/9/04	2275	27.4	0.34	0.25	0.08	1.03	0.35	0.47	0.47	0.77
Lena	6/5/04	61408	257.8	1.28	0.24	0.08	1.71	0.16	0.16	0.16	0.33
Lena	6/7/04	90720	189.8	0.90	0.24	0.08	1.42	0.16	0.16	0.22	0.34
Lena	8/19/04	35500	26.9	0.30	0.23	0.08	1.06	0.43	0.58	0.51	0.81
Lena	8/24/04	31100	21.6	0.26	0.24	0.08	1.07	0.47	0.66	0.51	0.84
Lena	10/7/04	24800	24.4	0.31	0.28	0.09	1.13	0.55	0.37	0.25	0.60
Lena	10/10/04	26189	32.2	0.33	0.26	0.07	1.13	0.47	0.35	0.25	0.73
Lena	3/24/05	3947	35.1	0.30	0.38	0.19	1.13	0.61	0.35	0.25	0.44
Lena	5/27/05	53784	168.5	0.77	0.24	0.10	1.34	0.14	0.16	0.20	0.34
Lena	6/4/05	109800	144.6	0.74	0.25	0.09	1.25	0.18	0.18	0.21	0.33
Lena	8/6/05	45500	31.2	0.23	0.35	0.11	1.33	0.53	0.35	0.22	0.41
Lena	8/14/05	37700	32.9	0.28	0.39	0.19	1.62	0.70	0.35	0.19	0.32
Lena	10/9/05	23900	23.7	0.28	0.29	0.08	1.06	0.55	0.38	0.23	0.63
Lena	10/10/05	23200	28.1	0.34	0.27	0.13	0.80	0.71	0.38	0.26	0.32
Kolyma	6/11/04	17300	94.8	0.68	0.44	0.14	1.42	0.27	0.23	0.23	0.44
Kolyma	6/15/04	15020	76.7	0.62	0.58	0.23	1.96	0.43	0.27	0.21	0.35
Kolyma	6/25/04	11700	28.1	0.34	0.40	0.11	1.29	0.42	0.35	0.20	0.64
Kolyma	7/15/04	7140	21.9	0.28	0.44	0.12	1.14	0.53	0.40	0.16	0.70
Kolyma	8/10/04	4810	8.7	0.16	0.37	0.11	1.20	0.81	0.61	0.24	0.74
Kolyma	8/25/04	6200	14.1	0.25	0.38	0.10	1.21	0.61	0.48	0.26	0.82
Kolyma	9/23/04	3000	8.0	0.14	0.37	0.12	1.19	0.72	0.60	0.24	0.66
Kolyma	4/22/05	ND	6.5	0.20	0.25	0.10	1.14	0.83	1.15	0.55	0.83
Kolyma	6/30/05	ND	13.6	0.21	0.36	0.09	0.93	0.54	0.42	0.19	0.78
Kolyma	7/19/05	ND	9.2	0.15	0.36	0.10	1.12	0.72	0.48	0.12	0.91
Kolyma	8/14/05	ND	19.4	0.29	0.41	0.10	0.96	0.47	0.37	0.16	0.60
Kolyma	8/27/05	ND	40.9	034	0.53	0.18	1.54	0.57	0.30	0.23	0.41
Kolyma*	9/12/05	ND	3.1	0.04	0.11	0.05	0.81	0.07	0.92	0.74	3.86
Kolyma*	9/29/05	ND	4.6	0.06	0.27	0.06	1.02	0.04	0.50	0.53	3.17

*samples measured on Varian GC/MS

Mackenzie River

Dissolved Organic Carbon

As in the Yukon, the DOC concentrations increase to their maximum values (4.9, 5.7 mg L^{-1} for 2004, 2005 respectively) at peak discharge and decrease thereafter to their minimal values (3.0, 3.3 mg L^{-1} for 2004, 2005 respectively) during low and baseflow (Figure 7a; Table 5). There is a dip in DOC for the 8/9/05 sample to 4.4 mg L^{-1} which doesn't compare well to a_{375}, but does correspond to shifts in SUVA and lignin for the same sample. The discharge weighted average DOC concentration was 3.77 mg L^{-1} in 2004 and 4.79 mg L^{-1} in 2005 (Table 6). Estimated annual DOC export was 0.95 Tg in 2004 and 1.69 Tg in 2005 (Table 6). In 2004 the annual area weighted DOC export was 555 kg $km^{-2}yr^{-1}$, however, in 2005 was ~two times higher (988 kg $km^{-2}yr^{-1}$; Table 6). Both export estimates and the discharge weighted mean concentration were smallest from the Mackenzie compared to other rivers. Carbon concentrations followed the descending limb of the hydrograph, resulting in a more gradual decline than in the Yukon (Figure 7a). DOC concentrations in the Mackenzie were the lowest of all the six rivers.

Optical Properties

Overall the a_{375} followed the discharge (Figure 7b) more closely than DOC leading to a weaker relationship between the two (r^2=0.86; data not shown). SUVA values showed maximum values at peak discharge (2.47, 2.46 L(mg C)$^{-1}$ m^{-1} for 2004, 2005 respectively) and minimum at base flow (1.59, 1.98 L(mg C)$^{-1}$ m^{-1} for 2004, 2005 respectively); however, the 8/9/05 sample increased to 2.52 L(mg C)$^{-1}$ m^{-1} (Figure 7c). SUVA's at peak flow in the Mackenzie River, like the Yukon, are smaller than those from the Yenisei, Lena, and Kolyma but consistent across rivers at low flow. Spectral slopes agree well with SUVA's, increasing at peak flow (16.7, 17.4 μm^{-1}) then decreasing again at base flow (21.4, 21.5μm^{-1}; Figure 7d). Spectral slopes are similar to the Yukon and Eurasian rivers during freshet, however, the North American rivers had slightly larger S values than Eurasian rivers in the winter. The relationship of discharge to DOC, SUVA,

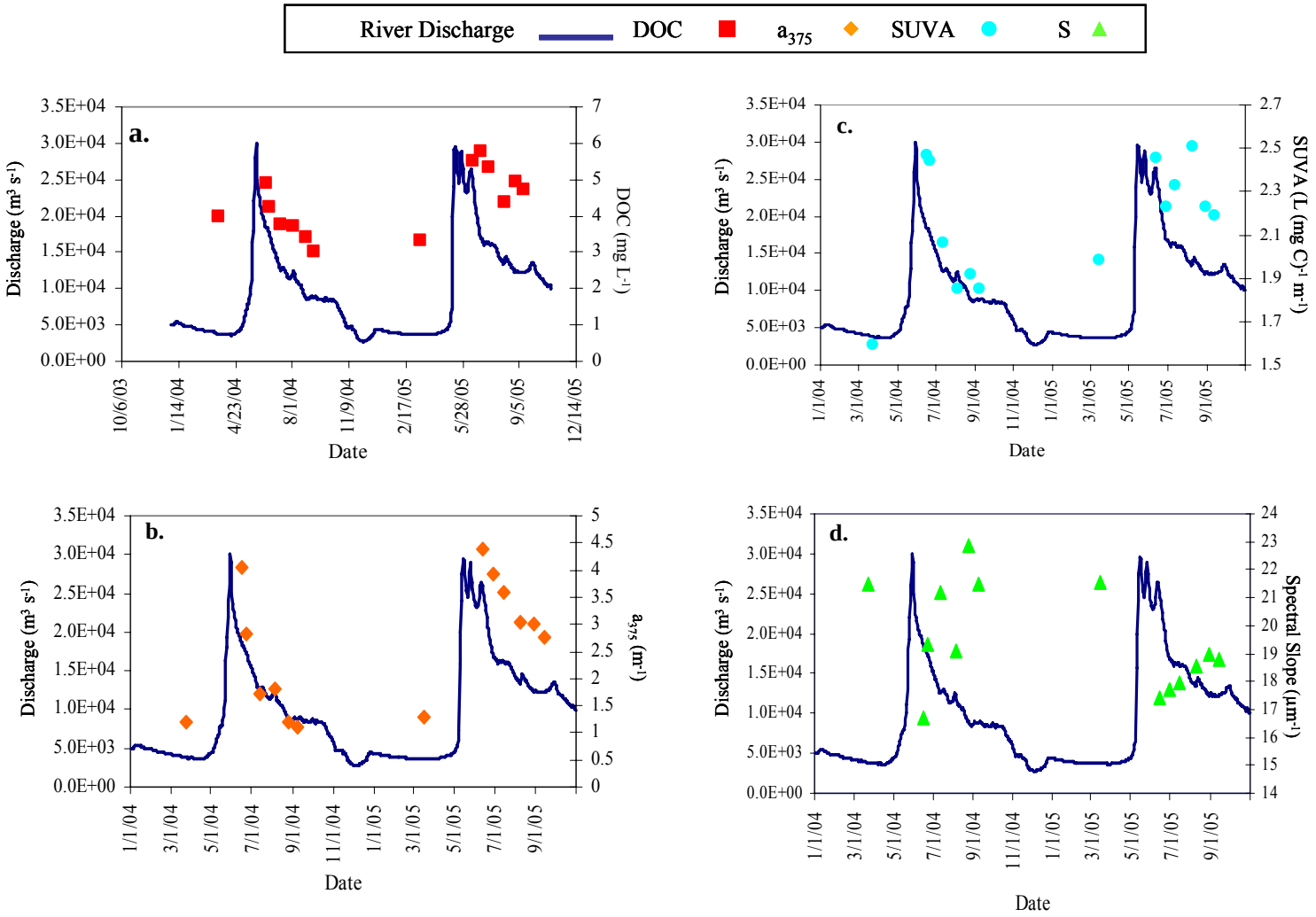

Figure 7. Mackenzie River discharge ($m^3\ s^{-1}$), a) Dissolved organic carbon (DOC; $mg\ L^{-1}$), b) Absorption coefficient at 375 nm (a_{375}; m^{-1}), c) Specific ultraviolet absorption coefficient (SUVA; $L(mg\ OC)^{-1}\ m^{-1}$) and d) Spectral slope (S; μm^{-1}) for the years 2004 and 2005.

and S was different from what we observed in the Yukon. DOC showed a weaker relationship to discharge while SUVA and S showed a stronger relationship to discharge (Figure 8). Fluorescence minima and maxima were found in the base and peak discharge samples, respectively in both 2004 and 2005 (Figure 9abcd). As in the Yukon, locations of fluorescence peaks did not change over the seasons but intensity did (Figure 9 and 10). The maximum fluorescence in the Mackenzie was about five times lower than in the Yukon. The base flow sample from 2005 had some scatter in the lower wavelengths (Figure 9c), but overall the locations of maximum fluorescence was similar to other rivers. The 8/9/05 sample described above has a slight enhancement of fluorescence at Ex:240, Em: 315-360 (Figure 10c) which corresponded to a drop in DOC but increased SUVA. Fluorescence peaks were found at Ex: 240, Em:425-475 and Ex:315, Em:400-475 in all samples from the Mackenzie River.

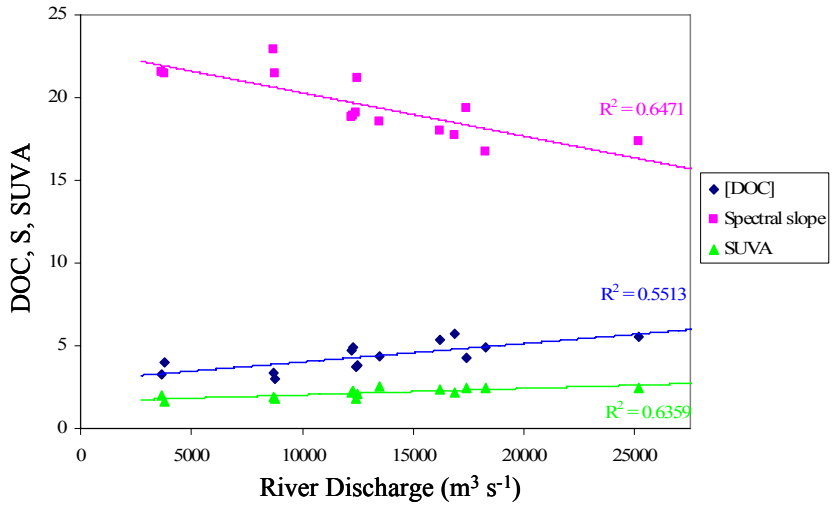

Figure 8. Relationship of Mackenzie discharge to DOC (mg L^{-1}), spectral slope (μm^{-1}), and SUVA (L (mg $OC)^{-1}$ m^{-1}).

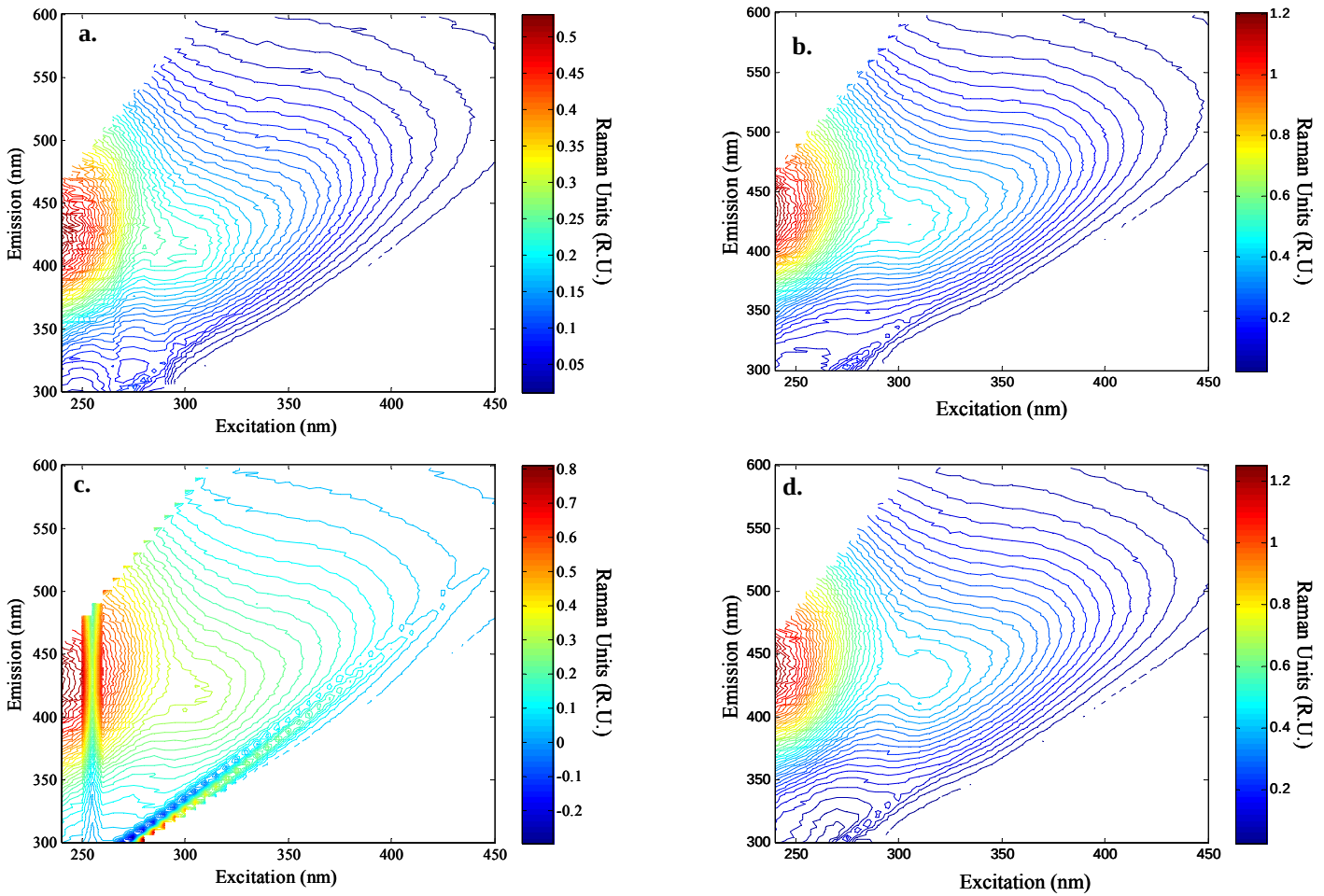

Figure 9. Fluorescence EEM's measured in Mackenzie samples from low flow (a,c) and peak flow (b,d) conditions in 2004 (upper panals) and 2005 (lower panals). Note each subplot is on a different scale.

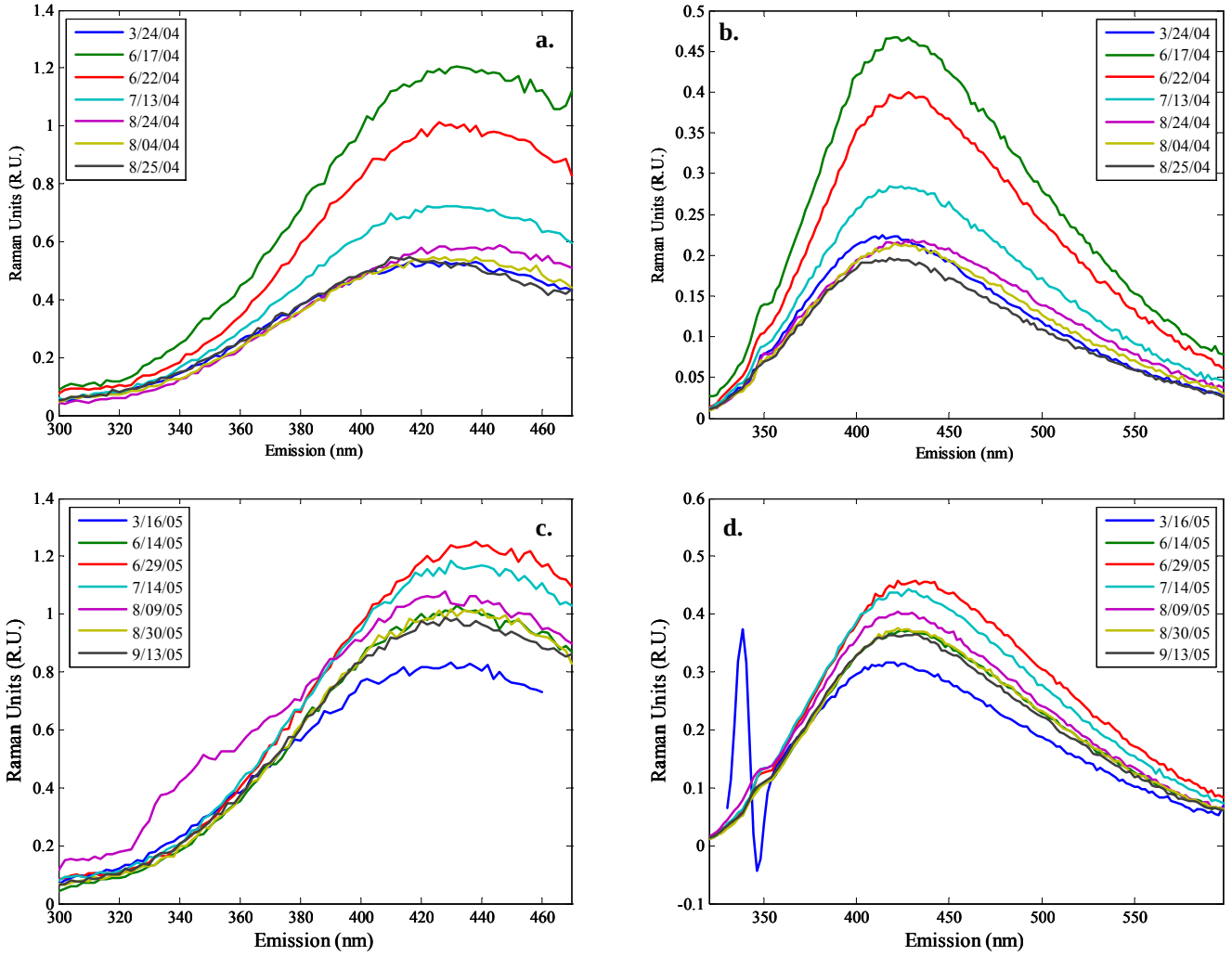

Figure 10. Seasonal variation in the maximum fluorescence intensity measured at excitation 240 nm (a & c) and 315 nm (b & d) for the Mackenzie River in 2004 (a & b) and 2005 (c & d).

Lignin Phenols

Lignin concentrations for 2004 reach their highest values slightly after peak discharge (Figure 11ab; Table 7). Lowest concentrations for 2004 were 2.7 μg L^{-1} (Σ8) and 0.6 mg LOP (100mg OC)$^{-1}$ (Λ8); while highest were 11.89 μg L^{-1} (Σ8) and 0.24 mg LOP (100mg OC)$^{-1}$ (Λ8). Maximum concentrations for 2005 were determined for the sample taken at peak flow (Σ8=10.12 μg L^{-1}, Λ8=0.16 mg LOP (100mg OC)$^{-1}$); and minimum during base flow (Σ8= 4.95 μg L^{-1}, Λ8=0.11 mg LOP (100mg OC)$^{-1}$) (Figure 11ab). Lignin concentrations were generally lowest from the Mackenzie than any of the other rivers, with the exception of the Yukon at base flow. Carbon-normalized yields were similar in the Mackenzie, Yukon, and Ob at base-flow, but at peak flow the Mackenzie was much lower than the Yukon and Ob. Compared to other rivers the (Ad/al)v changed the least in the Mackenzie, though a seasonal trend is still evident. Base flow has the lowest (ad/al)v (0.95, 0.75 for 2004, 2005 respectively) and peak flow showed the highest (ad/al)v (1.16, 1.16 for 2004, 2005 respectively) values for both 2004 and 2005 (Figure 11c). No apparent trend can be seen for (ad/al)s (Figure 11c). S/V and C/V ratios fluctuated seasonally (Figure 11d) with no clear trend which was commonly found in the other rivers. In 2004, CAD/FAD ratios are somewhat scattered; however, in 2005 they generally decrease from spring to fall (Figure 11e). PON/P values slightly increased throughout the 2004 sampling season while in 2005 the lowest values were at peak flow (Figure 11e). These were also similar to other rivers. No trend is apparent for DiBA/V in either years but data range from 0.41 to 0.95 (Figure 11f). These values are slightly elevated throughout the whole season, compared to the Yenisei, Lena and Kolyma but agree with the Yukon and Ob Rivers. As with optical properties the lignin phenol composition showed a lot more variability and weaker trends than the other rivers in this study.

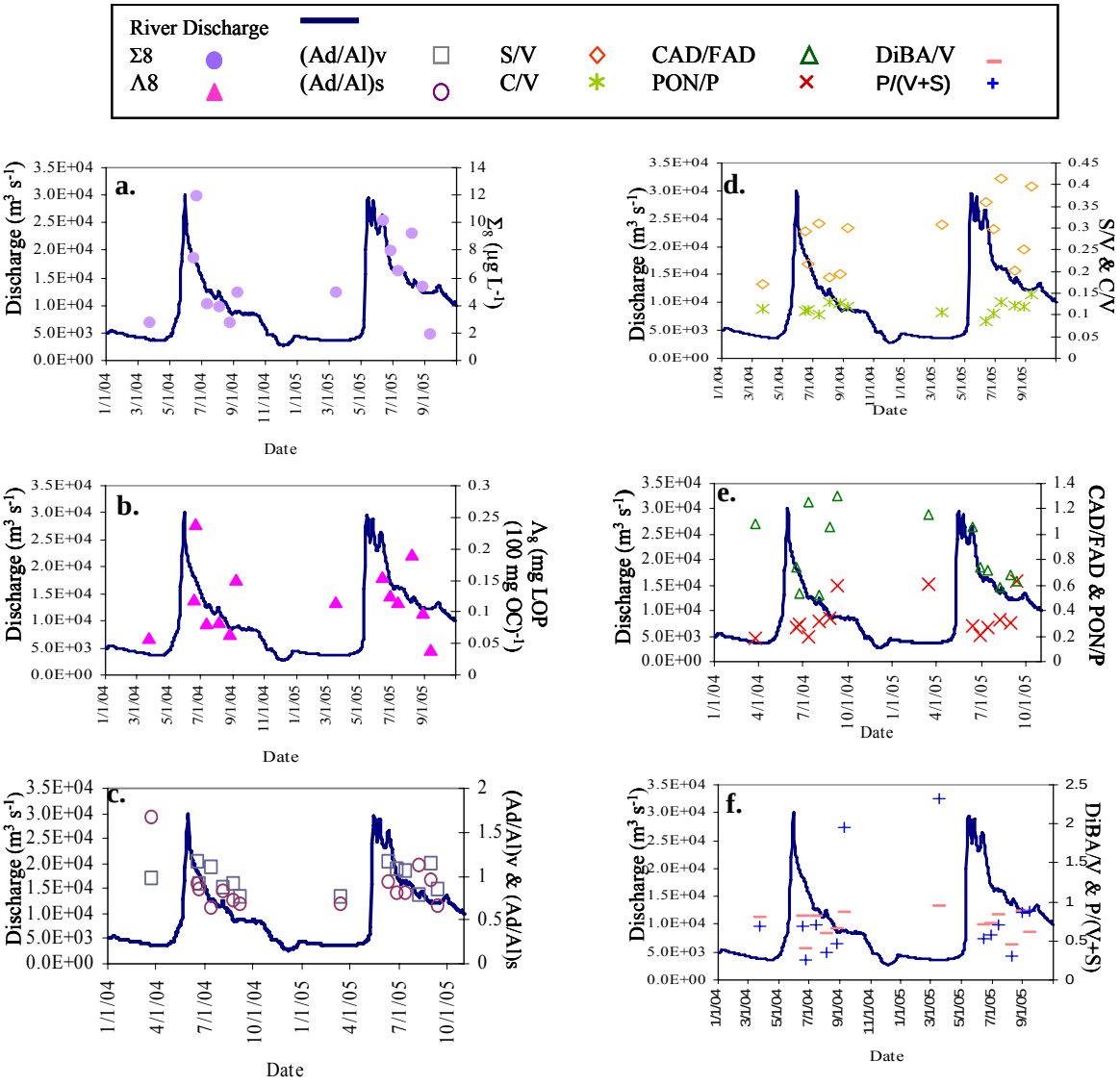

Figure 11. Mackenzie River discharge and a) Sigma 8 (Σ_8; μg/L), b) Lambda 8 (Λ_8; mg LOP/ 100 mg OC), c) Acid to aldehyde ratios for vanillyls and syringyls, d) Syringyls/Vanillyls (S/V) & Cinnamyls/ vanillyls (C/V), e) p-coumaric acid/ferulic acid (CAD/FAD) & p-hydroxybenzaldehyde/total p-hydroxy group (PON/P), f) 3,5-dihydroxybenzoic acid/vanillyl (DiBA/V) & total p-hydroxy group/(vanillyl + syringyl) (P/(V+S))

Ob River

Dissolved Organic Carbon

The Ob River shows a slightly different pattern of DOM export from the watershed. DOC reaches the highest concentrations in 2004 slightly after peak discharge (12.1 mg L^{-1}) (Figure 12a; Table 5), then decreases slightly but remains relatively high for the rest of the sampling season. In 2005, DOC was lowest while the river was frozen then increases post-breakup and remains between 11.2 and 12.7 mg L^{-1} for the rest of the season (Figure 12a). Discharge weighted average DOC concentrations are higher in the Ob than the Mackenzie and Yukon, totaling 9.33 mg L^{-1} in 2004 and 11.15 mg L^{-1} in 2005 (Table 6). Total annual DOC export was 3.24 Tg in 2004 and 3.99 Tg in 2005 (Table 6). Area weighted annual DOC export estimates for the Ob were 1260 kg $km^{-2}yr^{-1}$ in 2004 and 1552 kg $km^{-2}yr^{-1}$ in 2005 (Table 6) which were slightly less than the Yenisei but larger than the Kolyma and Mackenzie.

Optical Properties

The a_{375} seems to track the discharge somewhat better than DOC concentrations (Figure 12b; Table 5) though the relationship between the two is not as strong as in the other rivers studied (r^2=0.71; data not shown). For 2004 SUVA's, increase to the highest values (3.4 L(mg C)$^{-1}$ m^{-1}) (Figure 12c; Table 5) on the ascending limb of the hydrograph then decreased thereafter. In 2005 SUVA's increase from spring into early summer and reach the highest values (3.3 L(mg C)$^{-1}$ m^{-1}) on the descending limb of the hydrograph on 28 June (Figure 12c). Ob SUVA values are similar to those from the Lena and Yenisei at peak flow and to all rivers at base flow. Spectral slope trends are similar for both sampling seasons decreasing to the lowest values at peak discharge, and increasing again as the river returns to base flow (Figure 12d; Table 5). These values compare to other rivers in the spring but are somewhat smaller than the Yukon and Mackenzie at base flow. Spectral slopes seem to be the most sensitive indicator of discharge in the Ob (Figure 13). Fluorescence peaks were consistently in the same

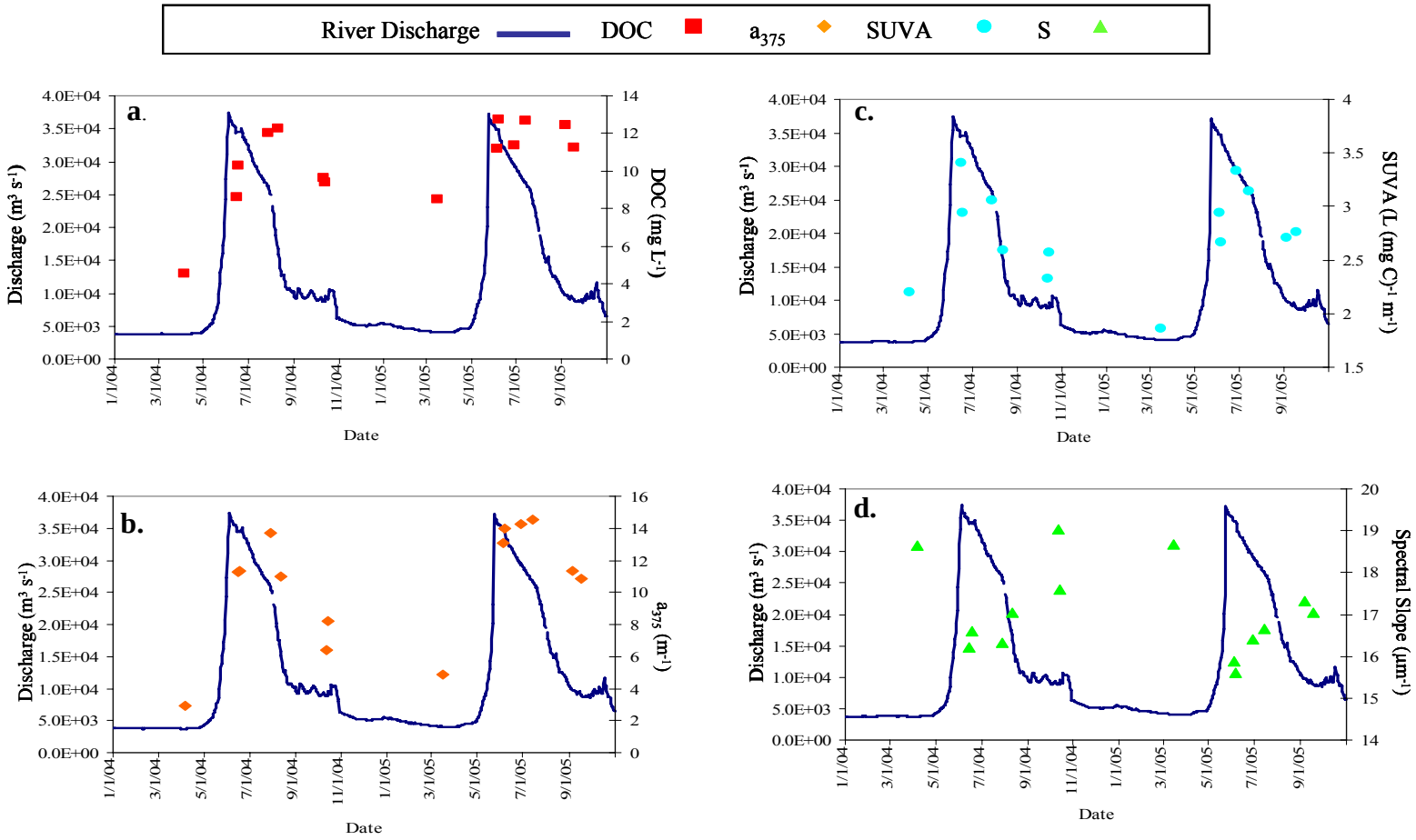

Figure 12. Ob River discharge ($m^3 s^{-1}$), and a) Dissolved organic carbon (DOC; mg L^{-1}), b) Absorption coefficient at 375 nm (a_{375}; m^{-1}), c) Specific ultraviolet absorption coefficient (SUVA; $L(mg\ OC)^{-1}m^{-1}$) and d) Spectral slope (S; μm^{-1}) for the years 2004 and 2005.

regions over the seasonal cycle located at Ex: 240, Em:425-475 and Ex:315, Em:400-475 (Figure 14 and 15). Minimum fluorescence intensities in 2004 occurred in late summer (corresponding to drop in (ad/al)v and increase in S/V; see below) and in 2005 at low flow (Figure 14ac). Maximum fluorescence occurred in July of both 2004 and 2005 (Figures 14bd). These maximum intensities corresponded to maximum DOC concentrations which was common across all rivers. Fluorescence intensity maximums were similar in the Ob to the Yukon and Yenisei (2005) but much larger than the Mackenzie.

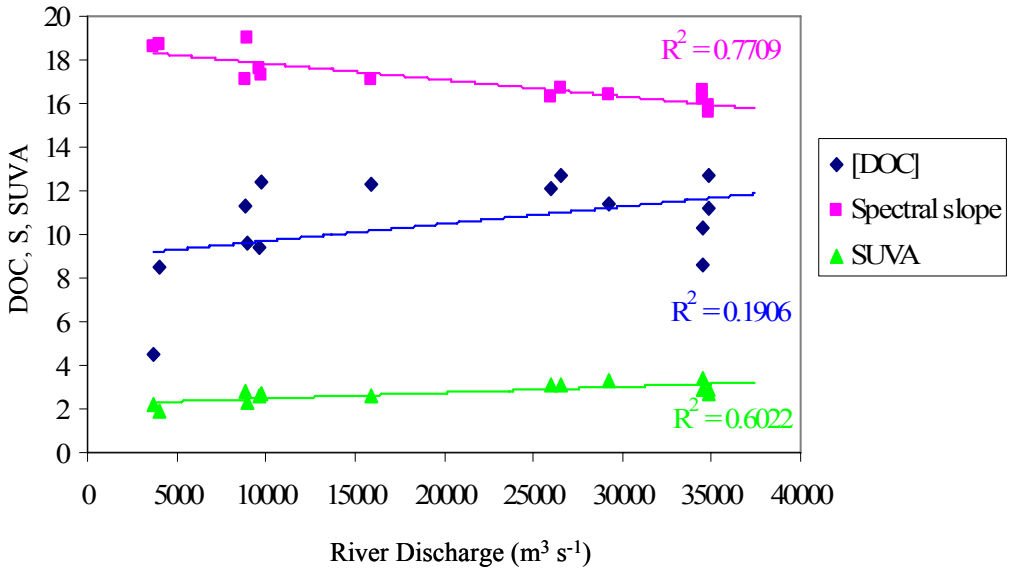

Figure 13. Relationship of Ob discharge to DOC (mg L^{-1}), spectral slope (μm^{-1}), and SUVA (L (mg OC)$^{-1}$ m^{-1}).

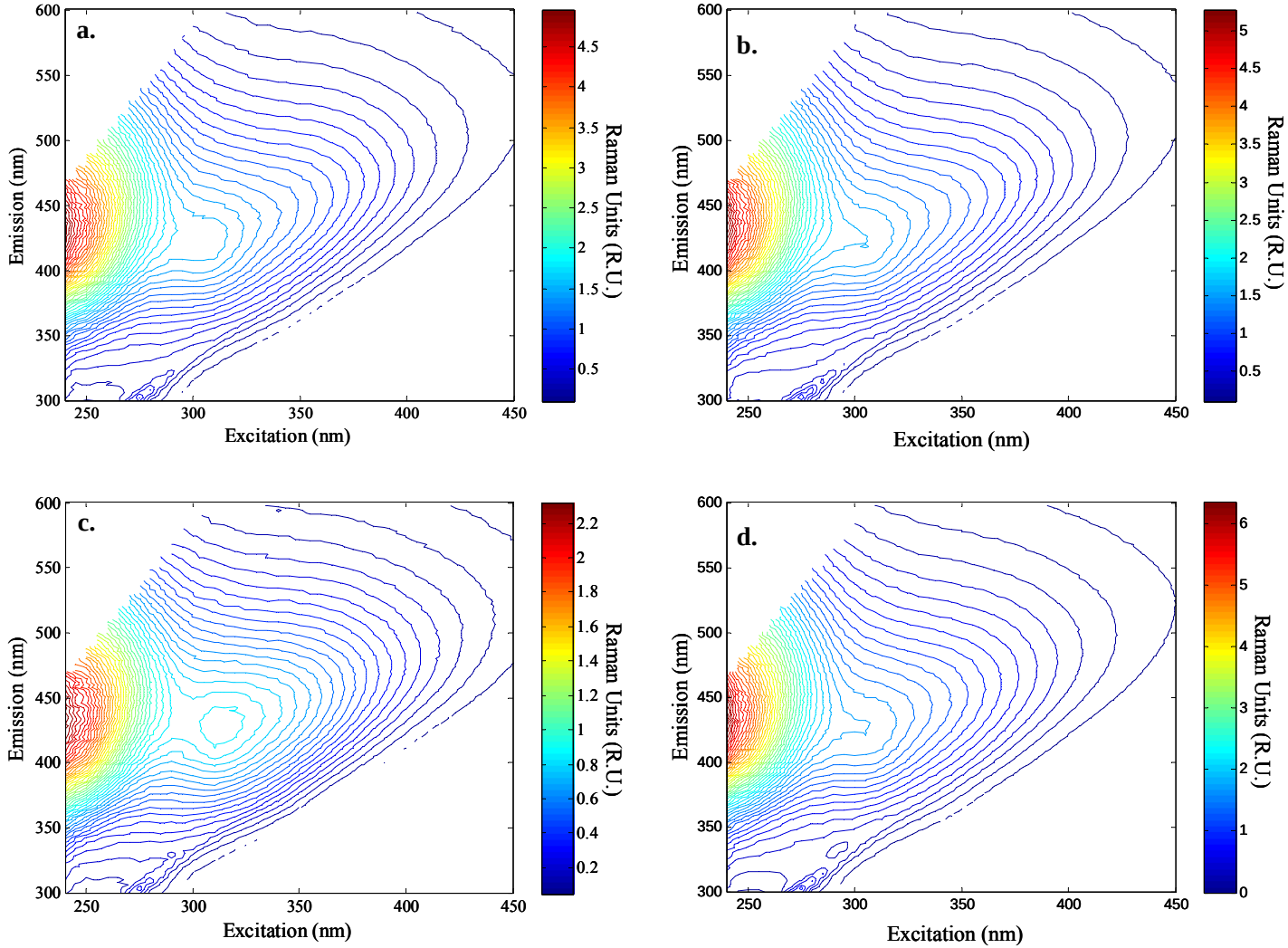

Figure 14. Fluorescence EEM's measured in Ob samples from low flow (a,c) and peak flow (b,d) conditions in 2004 (upper panals) and 2005 (lower panals). Note each subplot is on a different scale.

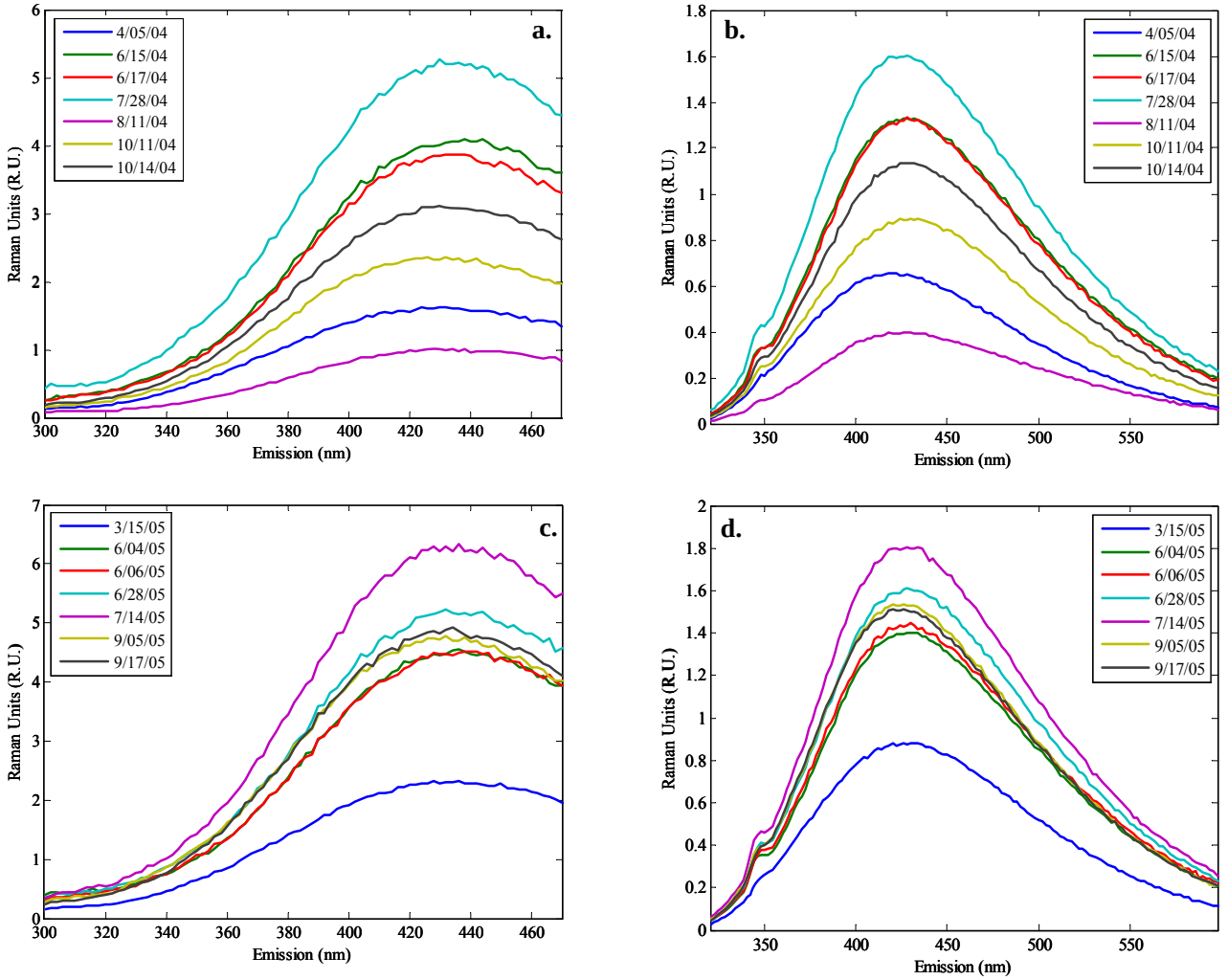

Figure 15. Seasonal variation in the maximum fluorescence intensity measured at excitation 240 nm (a & c) and 315 nm (b & d) for the Ob River in 2004 (a & b) and 2005 (c & d).

Lignin Phenols

Σ8 and Λ8 show the same trend of the greatest concentration of lignin phenols being discharged at peak flow (Figure 16ab; Table 7). Σ8 values at peak flow are much lower from the Ob than all other river with the exception of Mackenzie. At base flow they are much lower than the Lena, similar to the Kolyma, and slightly larger than the Mackenzie and Yukon Rivers. (Ad/al)v ratios have the same pattern as other rivers with the greatest values occurring at peak discharge (Figure 16c), however, similar to DOC concentrations they don't decrease as rapidly as in other rivers. The range of values are not significantly different than the other rivers. (Ad/al)s correspond well to S/V in 2004 and 2005, both show a more consistent pattern in the Ob than in other rivers (Figure 16). S/V ratios increase from base to peak flow in 2004 and reach their highest values on the descending limb of the hydrograph (Figure 16d). There is no clear pattern in S/V ratios for 2005, they appear relatively constant between 0.51 and 0.75 (Figure 16d). C/V ratios also showed no apparent trend and remained constant across both sampling seasons, ranging between 0.11 and 0.36 (Figure 16d). The S/V and C/V are elevated in the Ob compared to other rivers during late summer-early fall. A similar pattern is found for CAD/FAD ratios in both years with the lowest values occurring at peak flow increasing as the river returns to base flow (Figure 16e). These values seem to agree with the North American rivers better than the Yenisei, Lena, and Kolyma. The other Eurasian rivers are much lower at low flow and slightly lower in the spring than the Ob River. 2004, PON/P ratios are lowest on the descending limb of the hydrograph but in 2005 remain constant around 0.3 (figure 16e), similar to other rivers. DiBA/V generally increased during both sampling seasons reaching the highest values (1.19 and 1.49, for 2004 and 2005 respectively) late in the season (Figure 16f). P/V+S decrease from spring to early summer then increase again as the season progresses in both 2004 and 2005 (Figure 16f). Again the Ob's DiBA/V and P/(V+S) ratios are more similar to the North American rivers then the Yenisei, Lena, and Kolyma which overall have much lower values for both indicators.

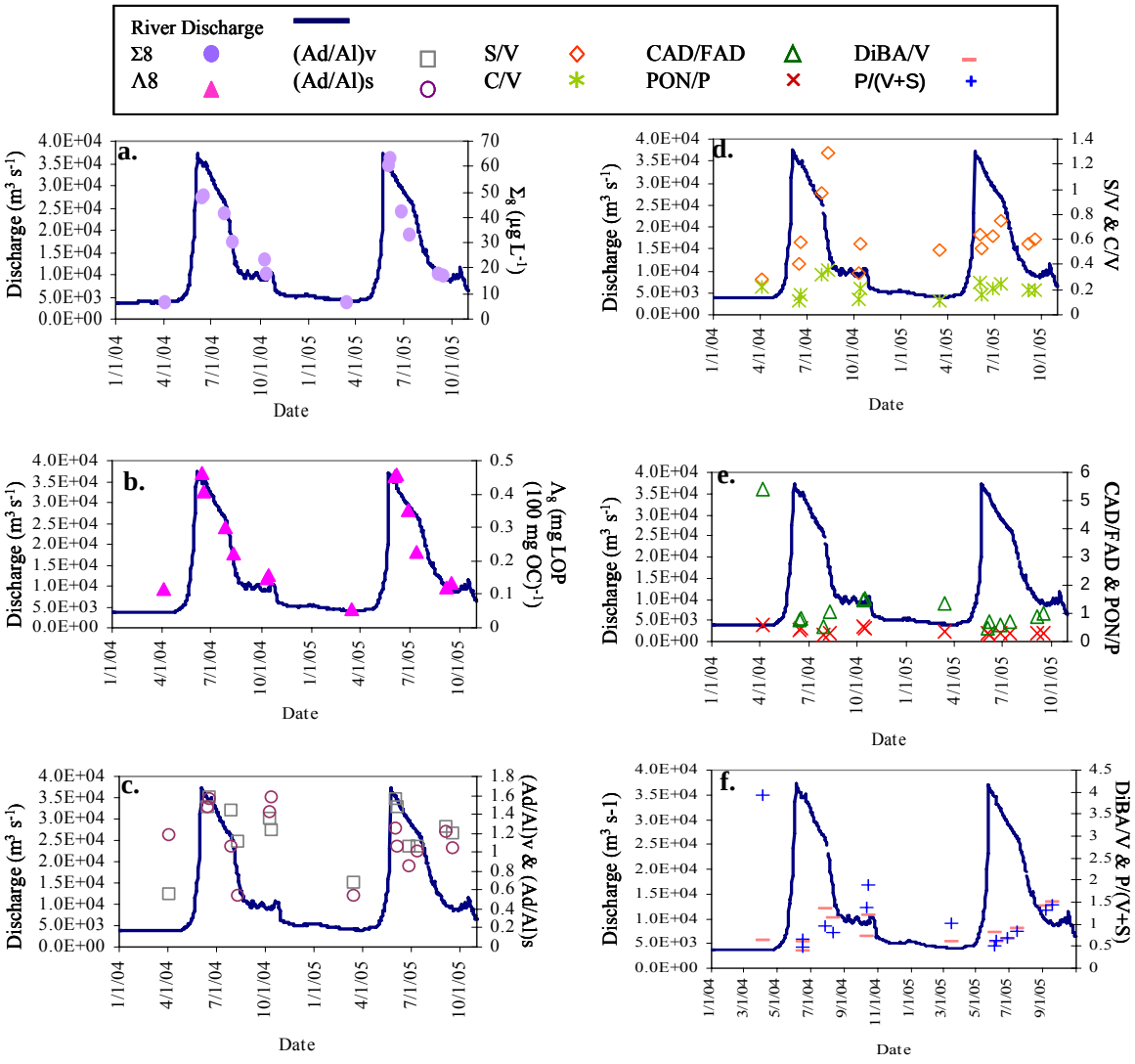

Figure 16. Ob River discharge and a) Sigma 8 (Σ_8; µg/L), b) Lambda 8 (Λ_8; mg LOP/ 100 mg OC), c) Acid to aldehyde ratios for vanillyls and syringyls, d) Syringyls/Vanillyls (S/V) & Cinnamyls/ vanillyls (C/V), e) p-coumaric acid/ferulic acid (CAD/FAD) & p-hydroxybenzaldehyde/total p-hydroxy group (PON/P), f) 3,5-dihydroxybenzoic acid/vanillyl (DiBA/V) & total p-hydroxy group/(vanillyl + syringyl) (P/(V+S))

Yenisei River

Dissolved Organic Carbon

The Yenisei River's hydrograph is the most dynamic of the rivers in this study hence DOM discharge followed a similar dynamic trend. Lowest DOC concentrations were found during the spring (2.5-3.0 mg L^{-1}) increasing to the highest concentrations during peak flow (15.0, 13.3 mg L^{-1} for 2004 and 2005 respectively) then dropping off abruptly post flood (Figure 17a; Table 5). Discharge weighted annual mean DOC concentrations are 9.50 and 7.25 mg L^{-1}, translating to an annual DOC export of 6.12 and 4.47 Tg yr-1, for 2004 and 2005 respectively (Table 6). Discharge weighted DOC concentrations were slightly less than the Ob but the annual export was second largest of all the rivers. Annual area weighted DOC export estimates were second largest of all the rivers and was estimated at 2372 and 1732 kg $km^{-2}yr^{-1}$ for 2004 and 2005, respectively (Table 6).

Optical Properties

As in the other rivers, the a_{375} tracked the discharge well and was strongly related to DOC (r^2=0.94; Figure 17b). Apparent trends were seen for both SUVA and S across sampling seasons. SUVA's, similar to other rivers were highest at peak flow (3.2-3.7 $L(mg\ C)^{-1}\ m^{-1}$) while S's were lowest (15.3-15.5 μm^{-1}) at peak flow (Figures 17cd; Table 5). SUVA's were similar to the Lena and Ob which were somewhat higher than the North American rivers at peak flow but consistent across rivers at base flow. S's are similar across all Eurasian rivers and are somewhat smaller than the Yukon and Mackenzie. The relationship between DOC and discharge is somewhat stronger than SUVA or S (Figure 18). A similar fluorescence pattern was found in the Yenisei as other rivers. Maximum fluorescence occurs at peak flow at Ex:240, Em:425-475 with a secondary peak at Ex:315, Em:400-475 (Figure 19abcd). Fluorescence intensity increases approximately 9 fold in 2004 and 6 fold in 2005 between base flow and peak flow (Figures 20abcd), but there were no apparent shifts in peak locations. The

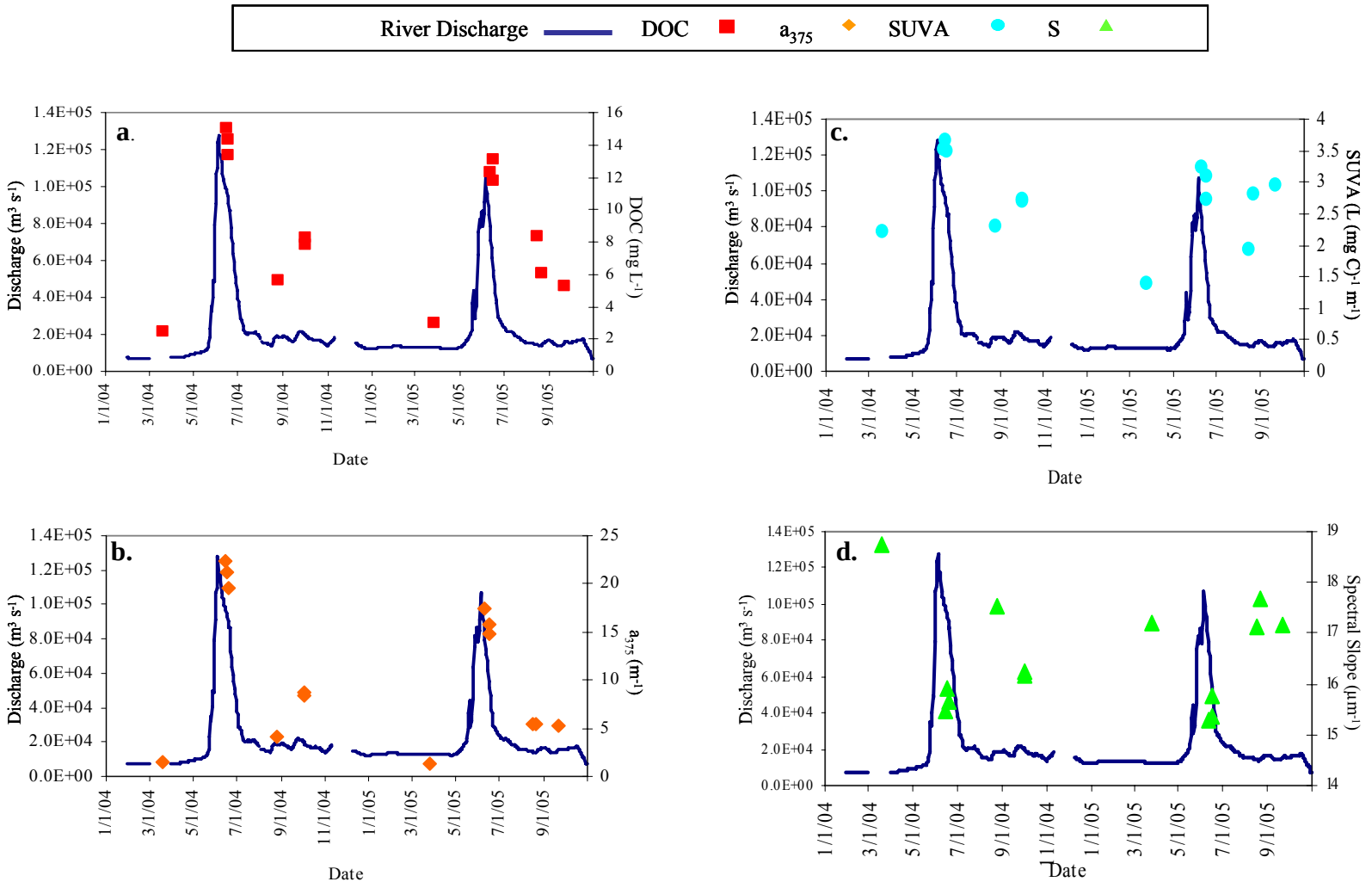

Figure 17. Yenisei River discharge ($m^3 s^{-1}$), and a) Dissolved organic carbon (DOC; mg L^{-1}), b) Absorption coefficient at 375 nm (a_{375}; m^{-1}), c) Specific ultraviolet absorption coefficient (SUVA; L(mg OC)$^{-1}m^{-1}$) and d) Spectral slope (S; μm^{-1}) for the years 2004 and 2005.

measured maximum fluorescence in the Yenisei was larger than all other rivers with the exception of Lena. The minimum fluorescence, along with the Yukon, was lower than the other rivers.

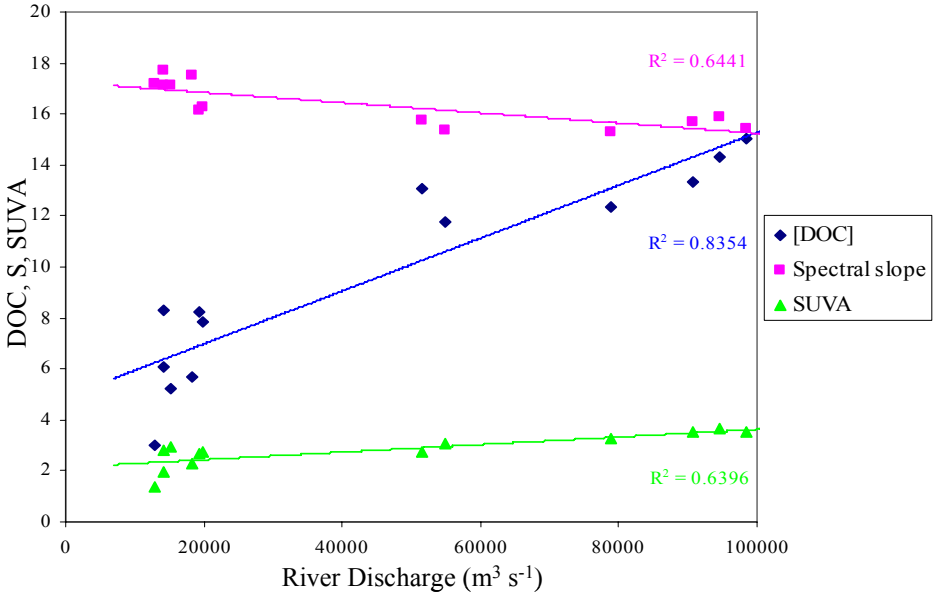

Figure 18. Relationship of Yenisei discharge to DOC (mg L^{-1}), spectral slope (μm^{-1}), and SUVA (L (mg OC)$^{-1}$ m^{-1}).

Lignin Phenols

Lignin, similar to optical properties showed vast differences between base flow and peak flow. Lignin concentrations where highest at peak flow (144.3 µg L^{-1}, 138.5 µg L^{-1} for 2004, 2005 respectively) decreasing to the lowest values at base flow (Figure 21a; Table 7). Lignin concentrations were larger than any other river with the exception of the Lena. Carbon normalized lignin yields showed similar patterns with peak flow reaching 0.85 and 0.97 mg LOP (100mg OC)$^{-1}$ (2004 and 2005, respectively) (Figure

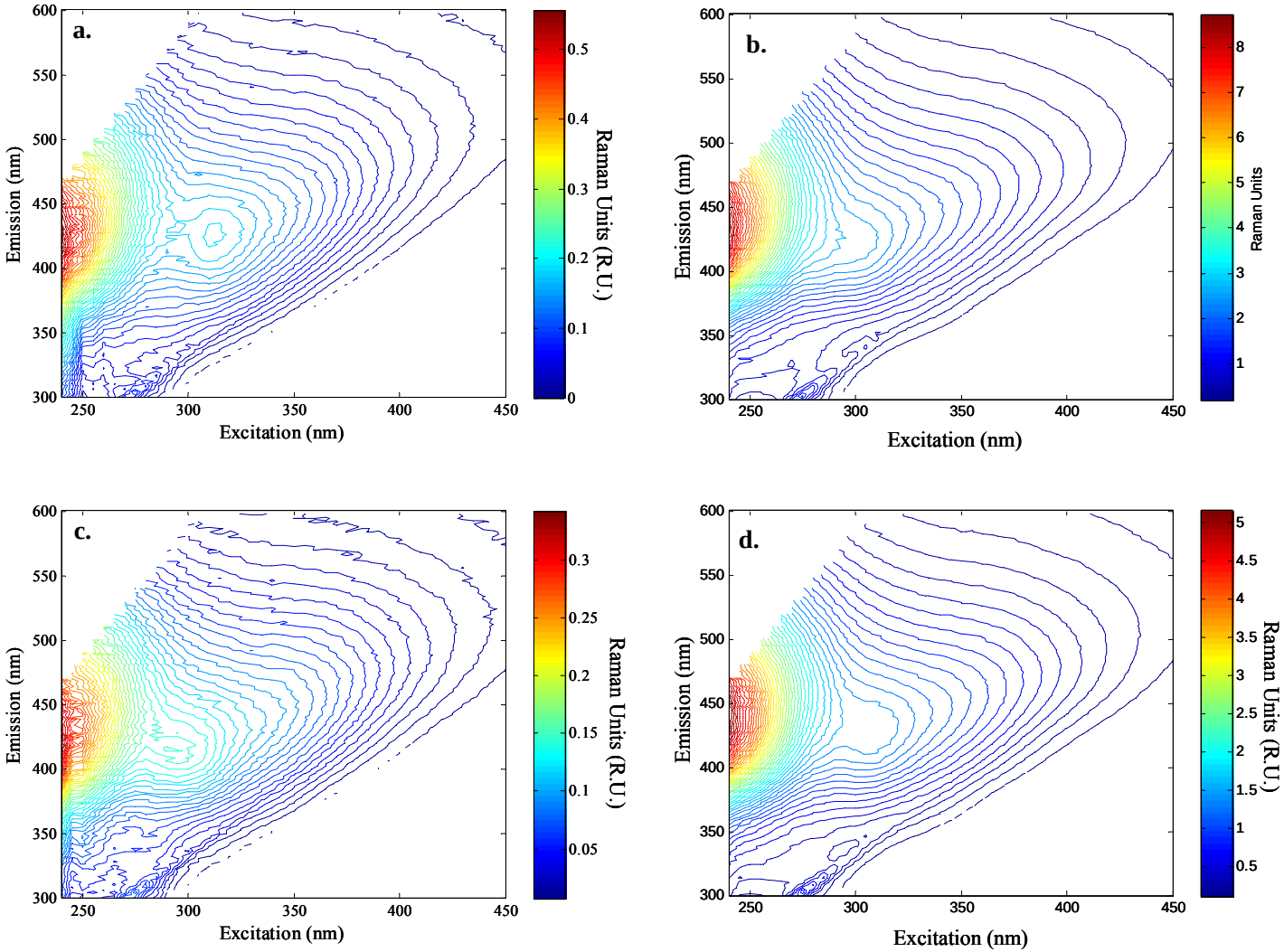

Figure 19. Fluorescence EEM's measured in Yenisei samples from low flow (a,c) and peak flow (b,d) conditions in 2004 (upper panals) and 2005 (lower panals). Note each subplot is on a different scale.

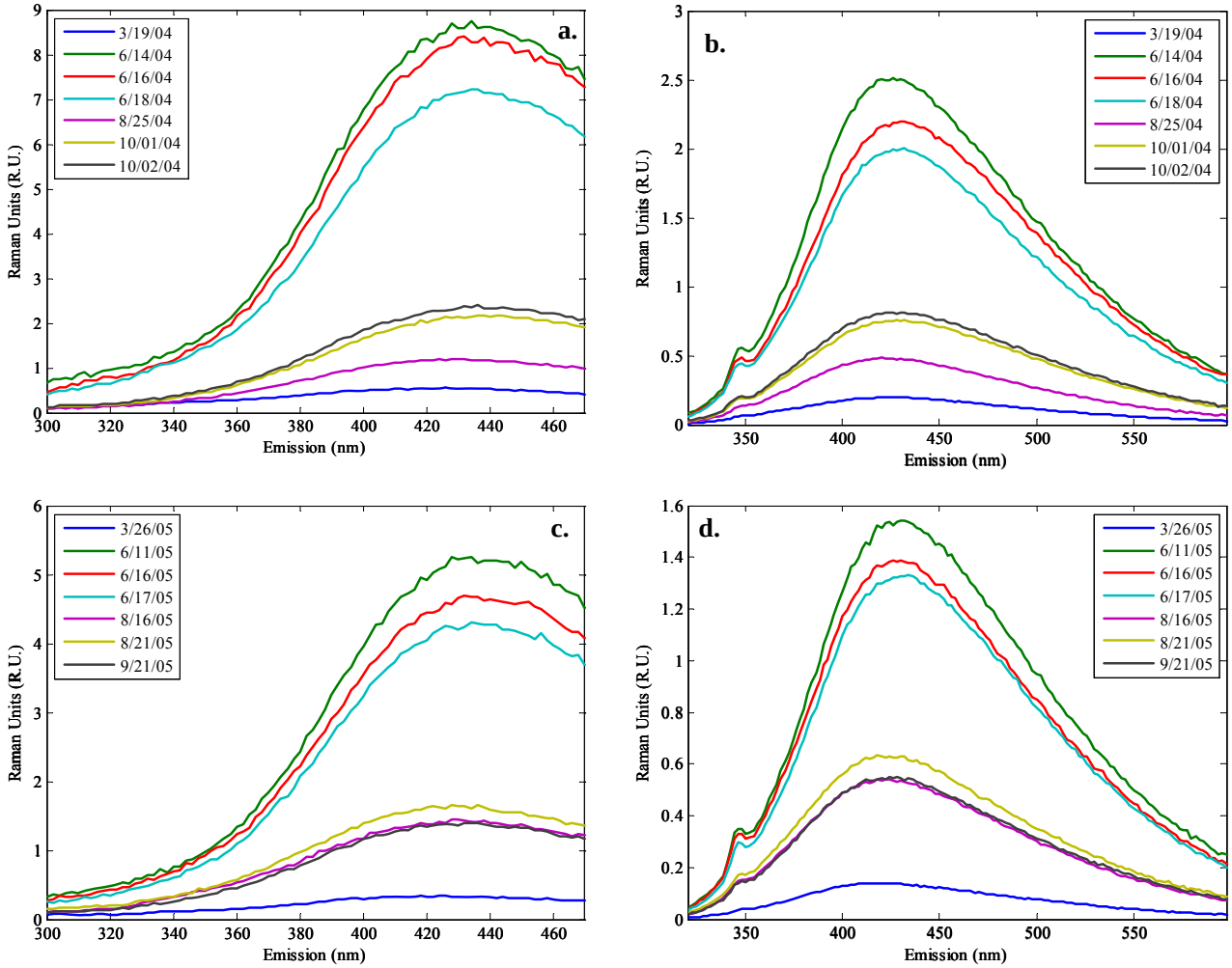

Figure 20. Seasonal variation in the maximum fluorescence intensity measured at excitation 240 nm (a & c) and 315 nm (b & d) for the Yenisei River in 2004 (a & b) and 2005 (c & d).

21b). Similar to Σ8, Λ8 was much higher than the Kolyma, Ob, Yukon and Mackenzie. In 2004 the Lena had much higher carbon-normalized yields than the Yenisei River but in 2005 the opposite was observed. Ratios of (ad/al)v increased similar to lignin concentrations, to the largest values (1.75, 1.56 for 2004, 2005 respectively) at peak discharge then decreased again post-flood (Figure 21c). Yenisei (ad/al)v ratios are seasonally comparable to all rivers. In 2004, (ad/al)s seem to follow (ad/al)v, however, in 2005 they are scattered (Figure 21c). No apparent trends were found in S/V ratios, and C/V remained constant around 0.09 in 2004 and 2005 (Figure 21d). Both ratios are similar in other rivers except the Ob which has slightly larger values. CAD/FAD ratios shift from lowest values (~0.3) at peak flow to higher values (~0.7) at base flow in 2004 (Figure 21e). A similar pattern was seen in 2005 though with higher variability (Figure 21e). PON/P ratios decreased from spring to early summer and increased again with progression of the season (Figure 21e). DiBA/V and P/(V+S) show similar patterns in 2004 and 2005 where lowest values occurred at peak flow then increase again as the river returns to base flow (Figure 21f). CAD/FAD, P/(V+S) and DiBA/V ratios in the Yenisei seem to more comparable to the Lena, and Kolyma than the Ob, Yukon, and Mackenzie.

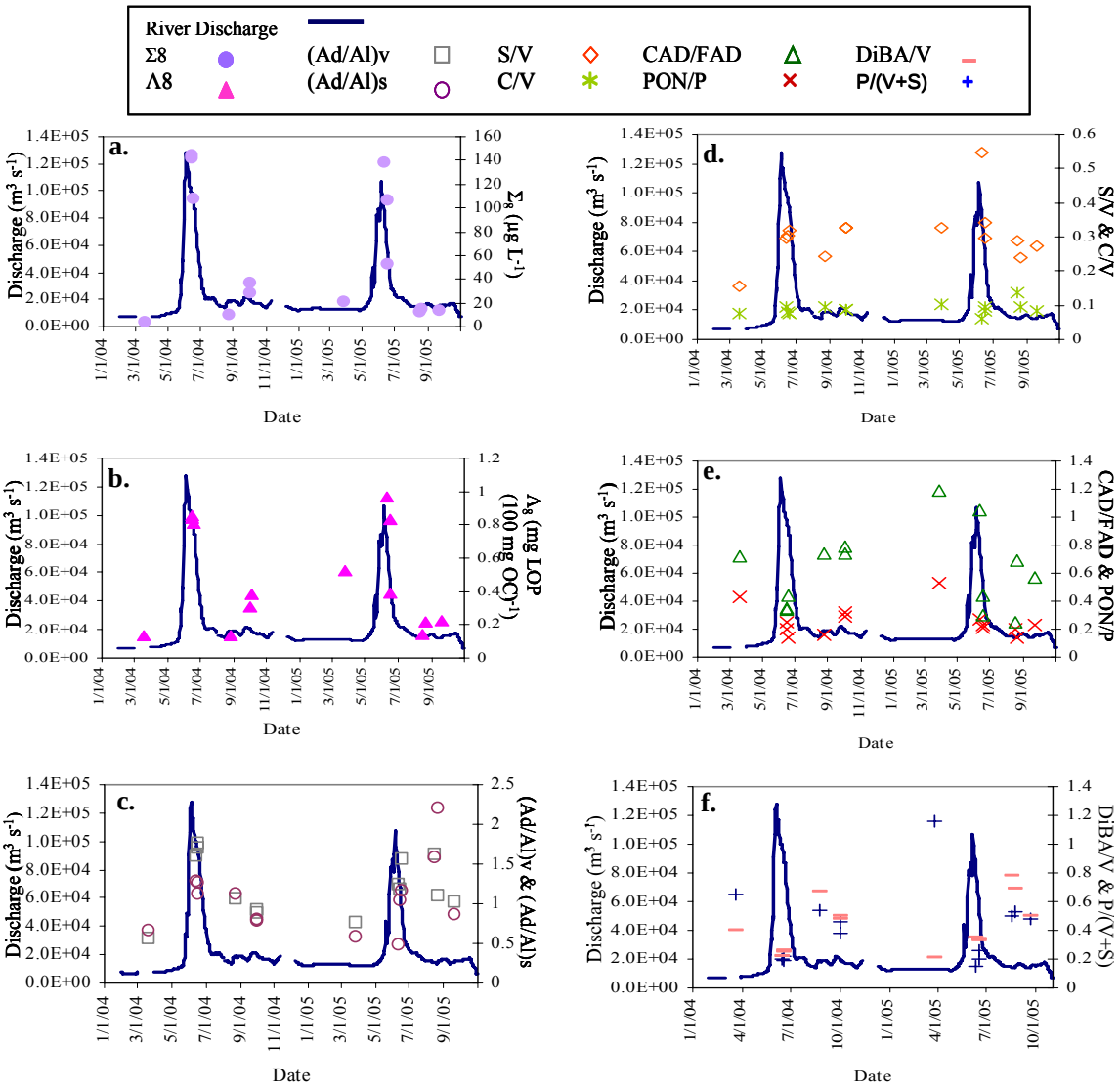

Figure 21. Yenisei River discharge and a) Sigma 8 (Σ_8; µg/L), b) Lambda 8 (Λ_8; mg LOP/ 100 mg OC), c) Acid to aldehyde ratios for vanillyls and syringyls, d) Syringyls/Vanillyls (S/V) & Cinnamyls/ vanillyls (C/V), e) p-coumaric acid/ferulic acid (CAD/FAD) & p-hydroxybenzaldehyde/total p-hydroxy group (PON/P), f) 3,5-dihydroxybenzoic acid/vanillyl (DiBA/V) & total p-hydroxy group/(vanillyl + syringyl) (P/(V+S))

Lena River

Dissolved Organic Carbon

Dissolved carbon concentrations, just as in the Yenisei River, increased dramatically from base flow (6.6 and 9.9 mg L^{-1} for 2004, 2005 respectively) to peak flow (18.2 and 19.2 mg L^{-1} for 2004, 2005 respectively) in both 2004 and 2005 and decreased thereafter (Figure 22a; Table 5). Discharge weighted annual mean DOC concentrations were 11.94 mg L^{-1}, and 13.46 mg L^{-1} in 2004 and 2005, respectively (Table 6). Annual DOC export estimates were 6.78 Tg and 8.93 Tg for 2004 and 2005 (Table 6). Discharge weighted DOC concentrations as well as annual export was larger in the Lena than any other river. Area weighted export estimates were 2801 kg DOC $km^{-2}yr^{-1}$ in 2004 and 3690 kg $km^{-2}yr^{-1}$ in 2005 which was also the highest of all the rivers (Table 6). The Lena has the highest DOC concentrations and contributes the most DOC to the Arctic ocean of the rivers studied here.

Optical Properties

As in the other rivers a_{375} followed the hydrograph closely and the relationship to DOC was as strong as it was for the Yenisei (r^2=0.92; Figure 22b; Table 5). In 2004 SUVA's increase at peak discharge from 2.9 L(mg C)$^{-1}$ m^{-1} at base flow to 3.7 L(mg C)$^{-1}$ m^{-1} at peak discharge then return to 2.8 L(mg C)$^{-1}$ m^{-1} post-flood (Figure 22c). In 2005, however, this same pattern was less evident. Spring and early summer samples had SUVA's between 2.8-2.9 L(mg C)$^{-1}$ m^{-1}, the values then dropped to between 2.2 and 2.7 L(mg C)$^{-1}$ m^{-1} in the late summer-early fall samples (Figure 22c). SUVA's are similar to the Ob and Yenisei at peak flow, and consistent across all rivers in the winter. The range between low and high values for the spectral slope data is small and data are scattered in 2004. The data ranged from 15.6 μm^{-1} on 7 June (6 days before peak river discharge) to 17.0 μm^{-1} on 24 Aug (Figure 22d). In 2005 there was a clear trend of decreasing spectral slopes from base (17.2 μm^{-1}) to peak flow (14.9 μm^{-1}), then as the river returns to base flow spectral slopes increased again (Figure 22d). Spectral slopes are slightly

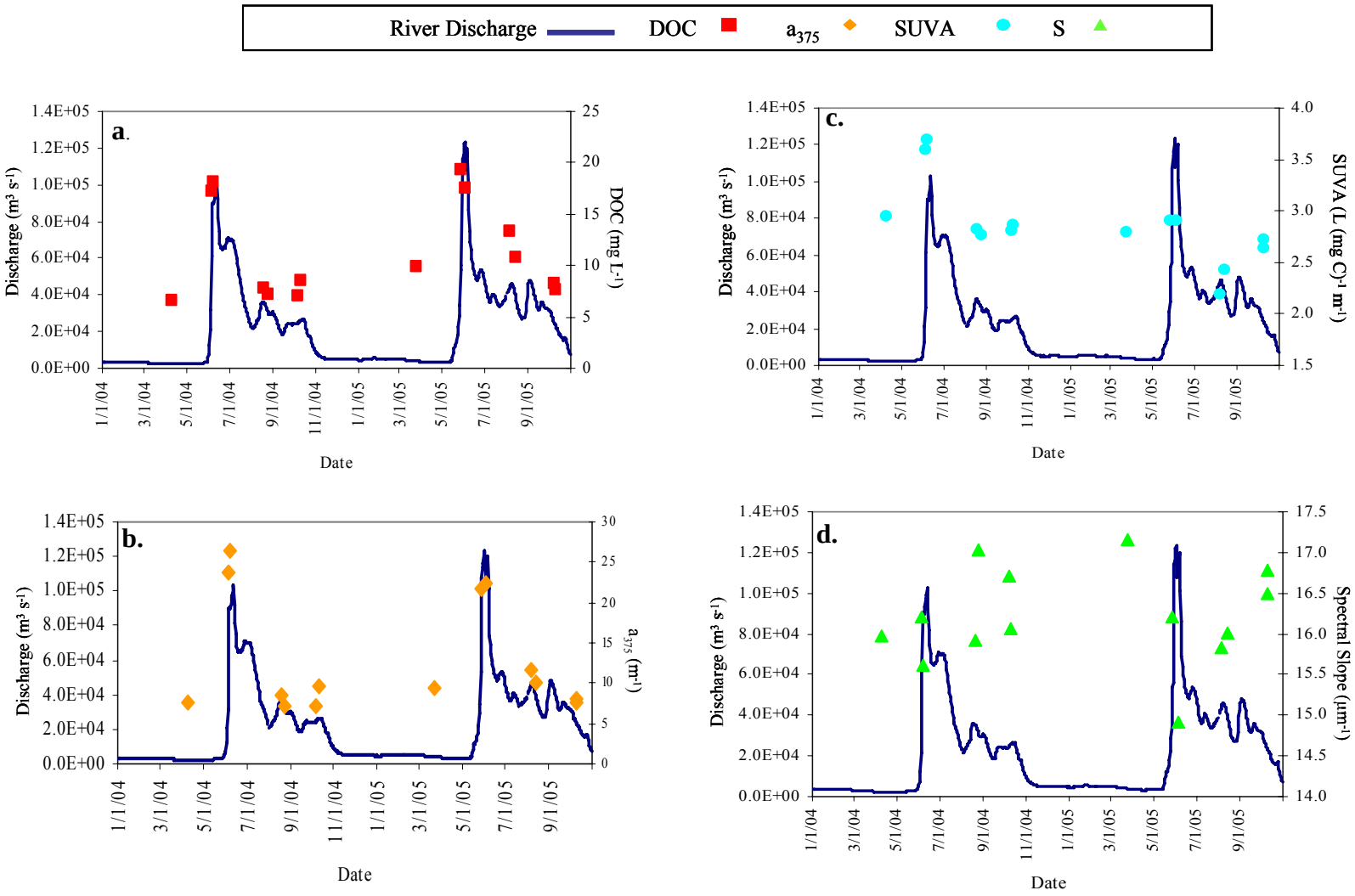

Figure 22. Lena River discharge ($m^3 s^{-1}$) and a) Dissolved organic carbon (DOC; mg L^{-1}), b) Absorption coefficient at 375 nm (a_{375}; m^{-1}), c) Specific ultraviolet absorption coefficient (SUVA; L(mg OC)$^{-1}$ m^{-1}) and d) Spectral slope (S; μm^{-1}) for the years 2004 and 2005.

smaller in the Lena than the North American rivers during the winter, but consistent across all rivers during freshet. DOC was the most sensitive to changes in hydrology, while SUVA responded very little (Figure 23). The Lena had the largest fluorescence measured of all rivers studied here. The maximum fluorescence intensity was measured in peak flow samples (6/07/04 and 5/27/05; Figures 24bd) and minimum in base flow samples (Figure 24ac). There was no shift in locations of maximum fluorescence which were the same as other rivers but there was a sharp contrast between fluorescence intensity at base flow and peak flow samples (Figures 25abcd). The minimum fluorescence intensity was similar to the Kolyma and Ob and significantly larger than Mackenzie, Yukon and Yenisei.

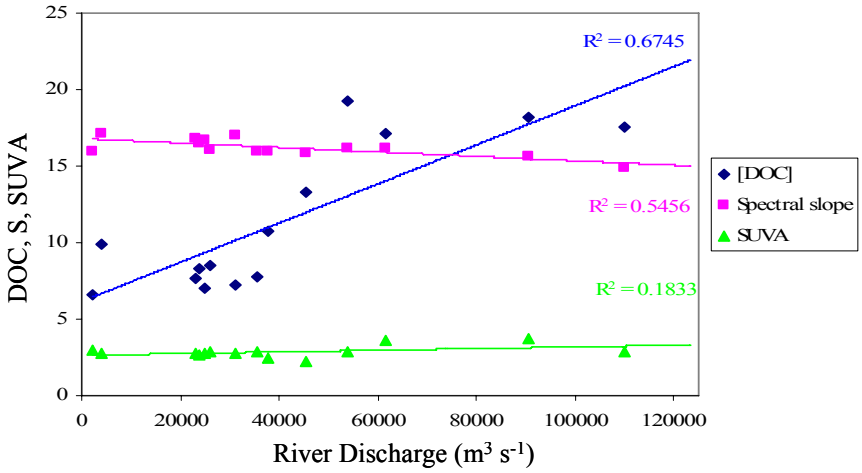

Figure 23. Relationship of Lena discharge to DOC (mg L^{-1}), spectral slope (μm^{-1}), and SUVA (L (mg $OC)^{-1}$ m^{-1}).

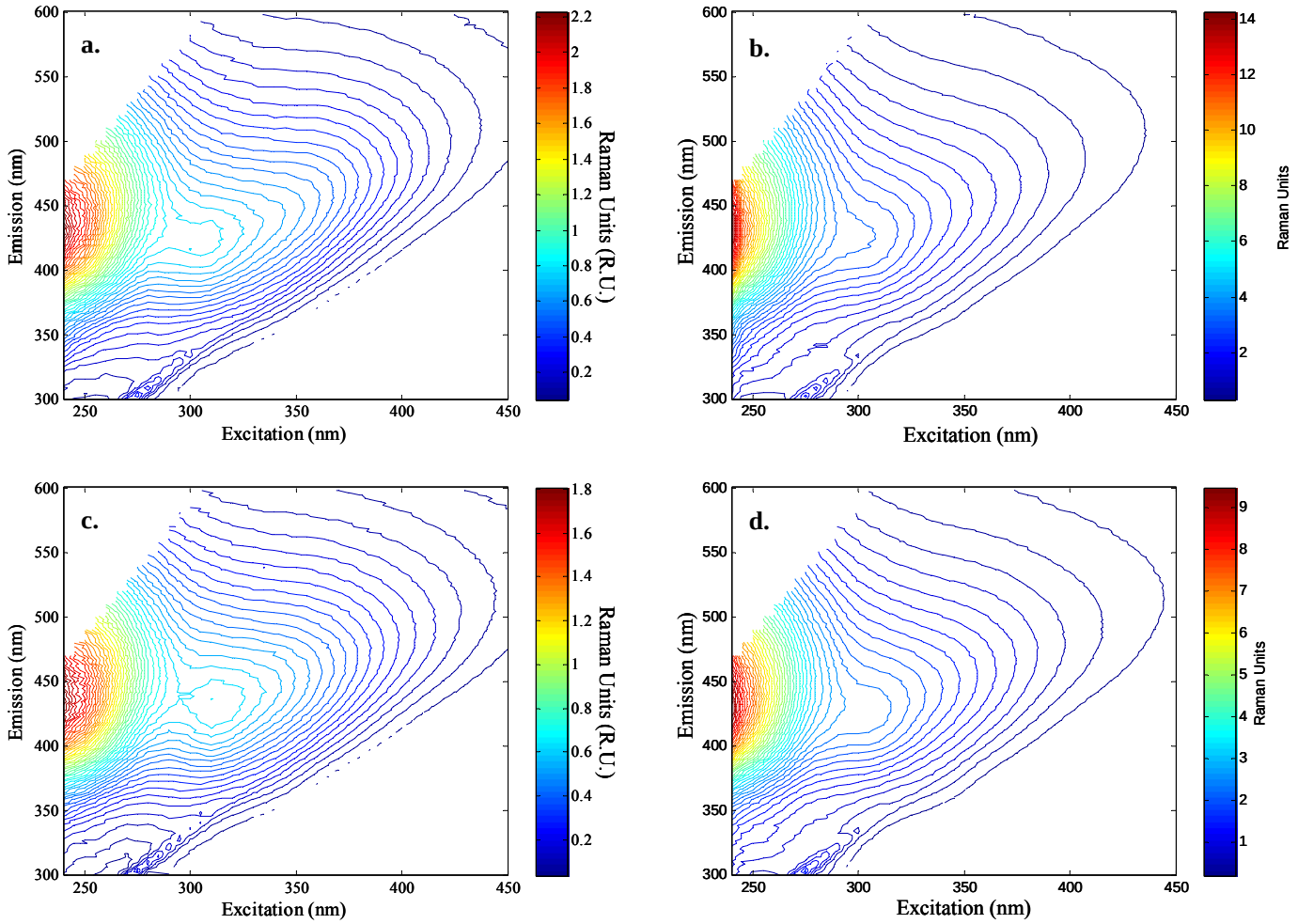

Figure 24. Fluorescence EEM's measured in Lena samples from low flow (a,c) and peak flow (b,d) conditions in 2004 (upper panals) and 2005 (lower panals). Note each subplot on a different scale.

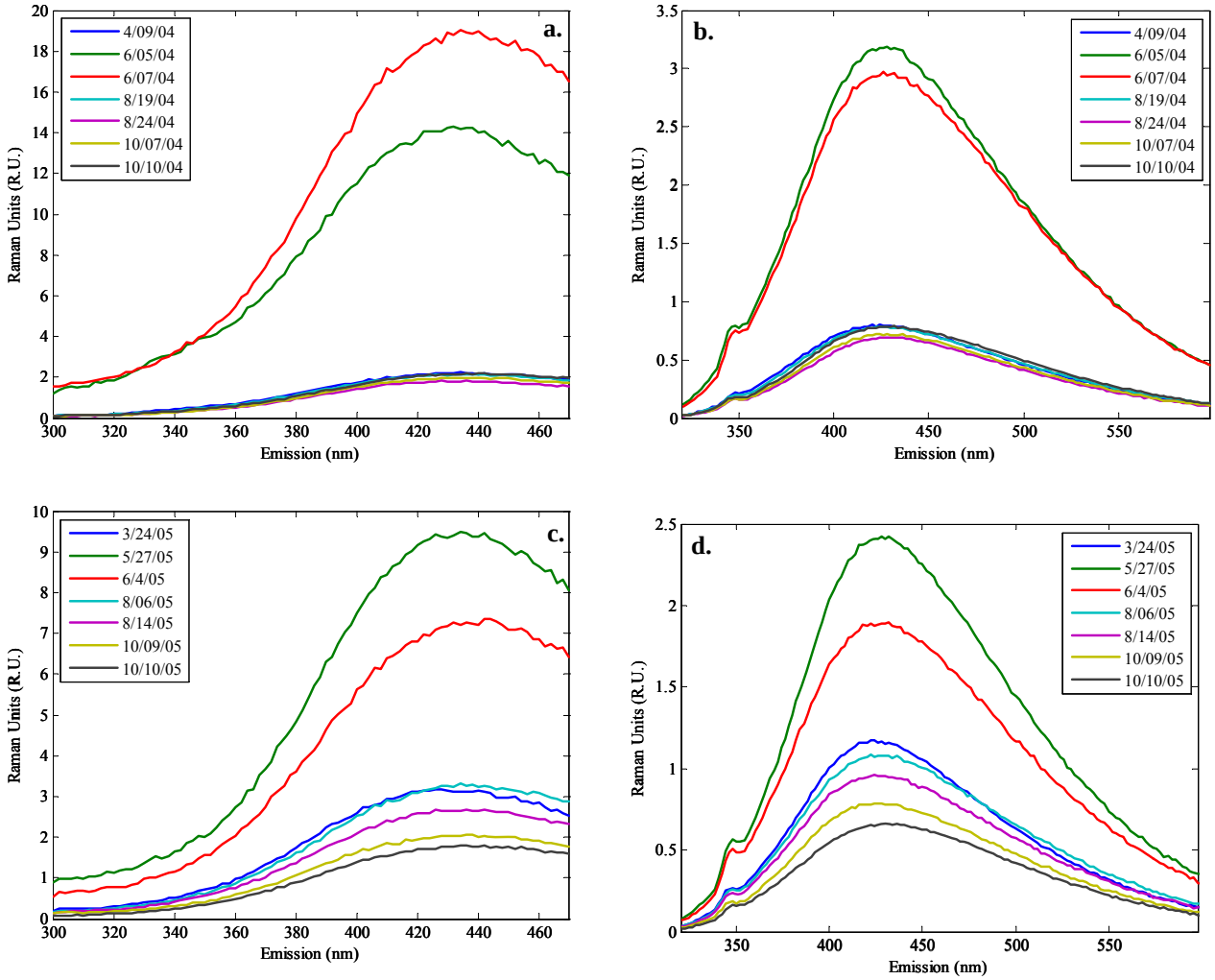

Figure 25. Seasonal variation in the maximum fluorescence intensity measured at excitation 240 nm (a & c) and 315 nm (b & d) for the Lena River in 2004 (a & b) and 2005 (c & d).

Lignin Phenols

LOP concentration increased dramatically from base flow ($\Sigma 8$=35.1 μg L^{-1}, $\Lambda 8$=0.30 mg LOP (100mg OC)$^{-1}$), to peak flow ($\Sigma 8$=168.5 μg L^{-1}, $\Lambda 8$=0.77 mg LOP (100mg OC)$^{-1}$) and dropped just as dramatically post flood ($\Sigma 8$=23.7-32.9 μg L^{-1}, $\Lambda 8$=0.23-0.34 mg LOP (100mg OC)$^{-1}$; Figure 26; Table 7). LOP concentrations measured on the Lena were higher than any other river at both base and peak flow. $\Lambda 8$ were also significantly higher in the Lena at base and peak flow than the other rivers (except in 2005 when the Yenisei was higher). In 2004 there is a shift from lower (1.03-1.13) to higher (1.42-1.71) (ad/al)v ratios at peak flow, though this trend is not as evident in 2005 (Figure 26c). There is a slight increase in (ad/al)v from 1.13 to 1.34 at peak flow in 2005, but they remain high late into the summer reaching the maximum values mid-Aug (1.62), until they dropped off back down to 0.80-1.06 early in the fall (Figure 26c). The range of (ad/al)v is similar to other rivers. (Ad/al)s show no clear pattern ranging from 0.8 to 1.4 (Figure 26c). S/V and C/V ratios in 2004 consistently range from 0.23 to 0.28 and 0.8 to 0.9, respectively (Figure 26d). In 2005 both S/V and C/V ratios decrease from base flow to peak flow, then increase again late in the season (Figure 26d). These ratios also are similar in other rivers, except the Ob River. CAD/FAD and PON/P ratios followed a similar pattern, in 2004 where lowest values were measured at peak discharge (Figure 26e). In 2005, both ratios remained fairly constant throughout the sampling season (Figure 26e). DiBA/V and P/(V+S) followed the same trend in 2004 and 2005 with lowest values at freshet and higher values at base flow (Figure 26f). Similar to the Yenisei, CAD/FAD, P/(V+S), and DiBA/V values are lower than the north American rivers.

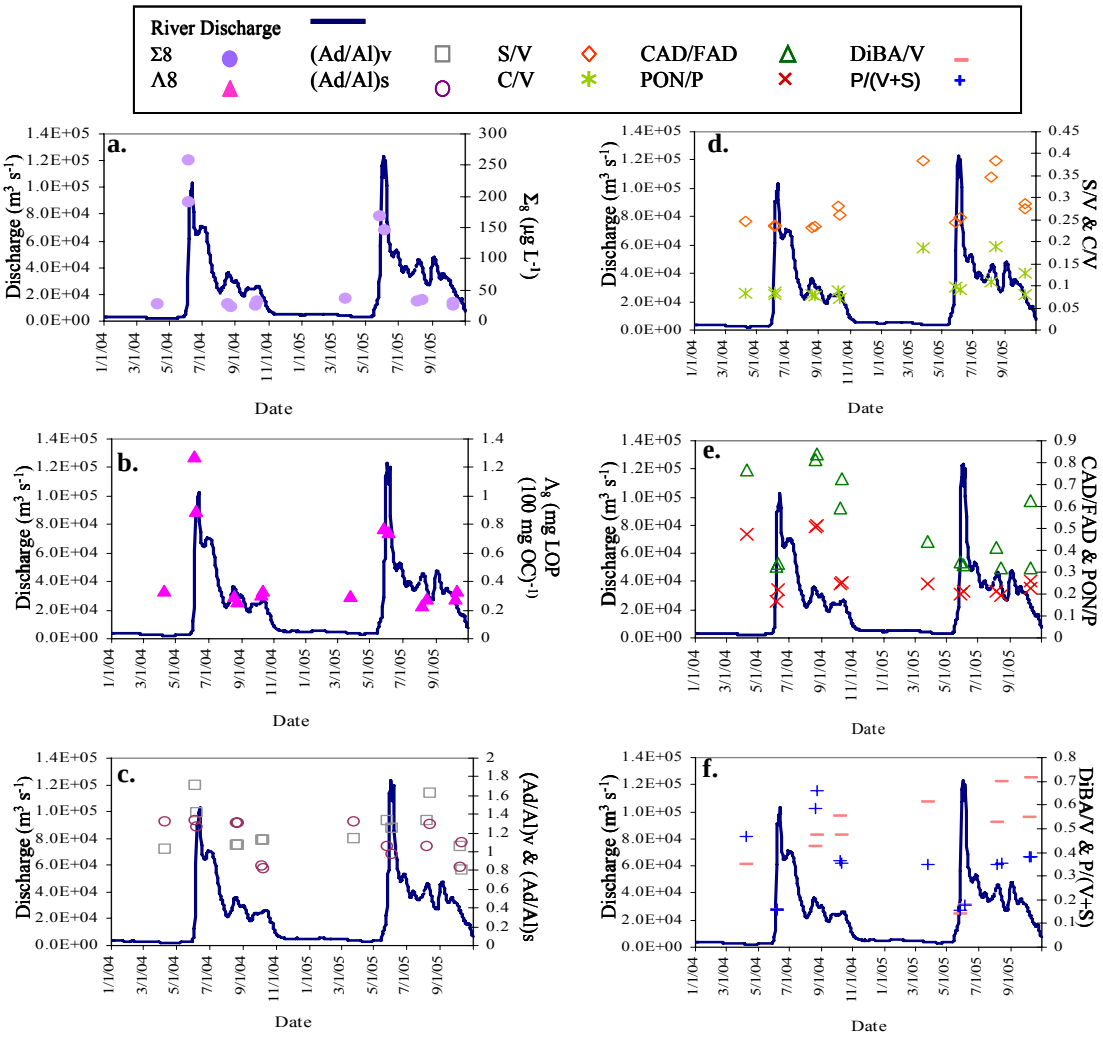

Figure 26. Lena River discharge and a) Sigma 8 (Σ_8; µg/L), b) Lambda 8 (Λ_8; mg LOP/ 100 mg OC), c) Acid to aldehyde ratios for vanillyls and syringyls, d) Syringyls/Vanillyls (S/V) & Cinnamyls/ vanillyls (C/V), e) p-coumaric acid/ferulic acid (CAD/FAD) & p-hydroxybenzaldehyde/total p-hydroxy group (PON/P), f) 3,5-dihydroxybenzoic acid/vanillyl (DiBA/V) & total p-hydroxy group/(vanillyl + syringyl) (P/(V+S))

Kolyma River

Dissolved Organic Carbon

In 2004 the first sample of the season was taken at peak discharge, DOC and a_{375} were therefore at their highest values and decreased thereafter (Figure 27ab; Table 5). Currently, 2005 discharge data is not available for the Kolyma. Assuming that peak flow occurred approximately the same time as in 2004 the second sample of the year (6/30/05) was most representative of peak flow. DOC increased from base flow to peak flow and rapidly declined as the river returned to base flow (Figure 27a). The discharge weighted annual mean DOC concentration was 7.32 mg L^{-1} DOC in 2004 and 8.13 mg L^{-1} DOC in 2005 (Table 6). Based on monthly averages, estimated annual DOC export was 0.72 Tg in 2004 and 0.88 Tg in 2005 (Table 6). Discharge weighted DOC concentrations were comparable to the Yukon and Yenisei while annual export was the smallest of all the rivers. Estimated area weighted DOC export in 2004 was 1074 kg DOC $km^{-2}yr^{-1}$ and in 2005 was 1313 kg $km^{-2}yr^{-1}$ (Table 6) which was the smallest of the Eurasian rivers.

Optical Properties

a_{375} showed a strong relationship with the hydrograph and DOC as in most other rivers (r^2=0.90; Figure 27ab; Table 5). SUVA's in 2004 decrease from the highest values (0.29 L(mg C)$^{-1}$ m^{-1}) at peak flow to lowest at base flow (2.2 L(mg C)$^{-1}$ m^{-1}; Figure 27c; Table 5). Spectral slopes show the opposite trend, increasing from peak flow (15.7 µm-1) to base flow (17.6 µm-1; Figure 27d). In 2005, SUVA's vary from 2.2 to 2.7 L(mg C)$^{-1}$ m^{-1} without any apparent trend and spectral slopes seemed to decrease from base flow to peak flow like in the other rivers (Figure 27cd; Table 5). Values for SUVA's and S are similar for the other Eurasian rivers. The relationship between discharge and DOC is particularly strong in the Kolyma (Figure 28); however, because discharge data was not available after October of 2004 this is based on fewer data points. In 2004 and 2005, maximum fluorescence intensity was measured on the sample most

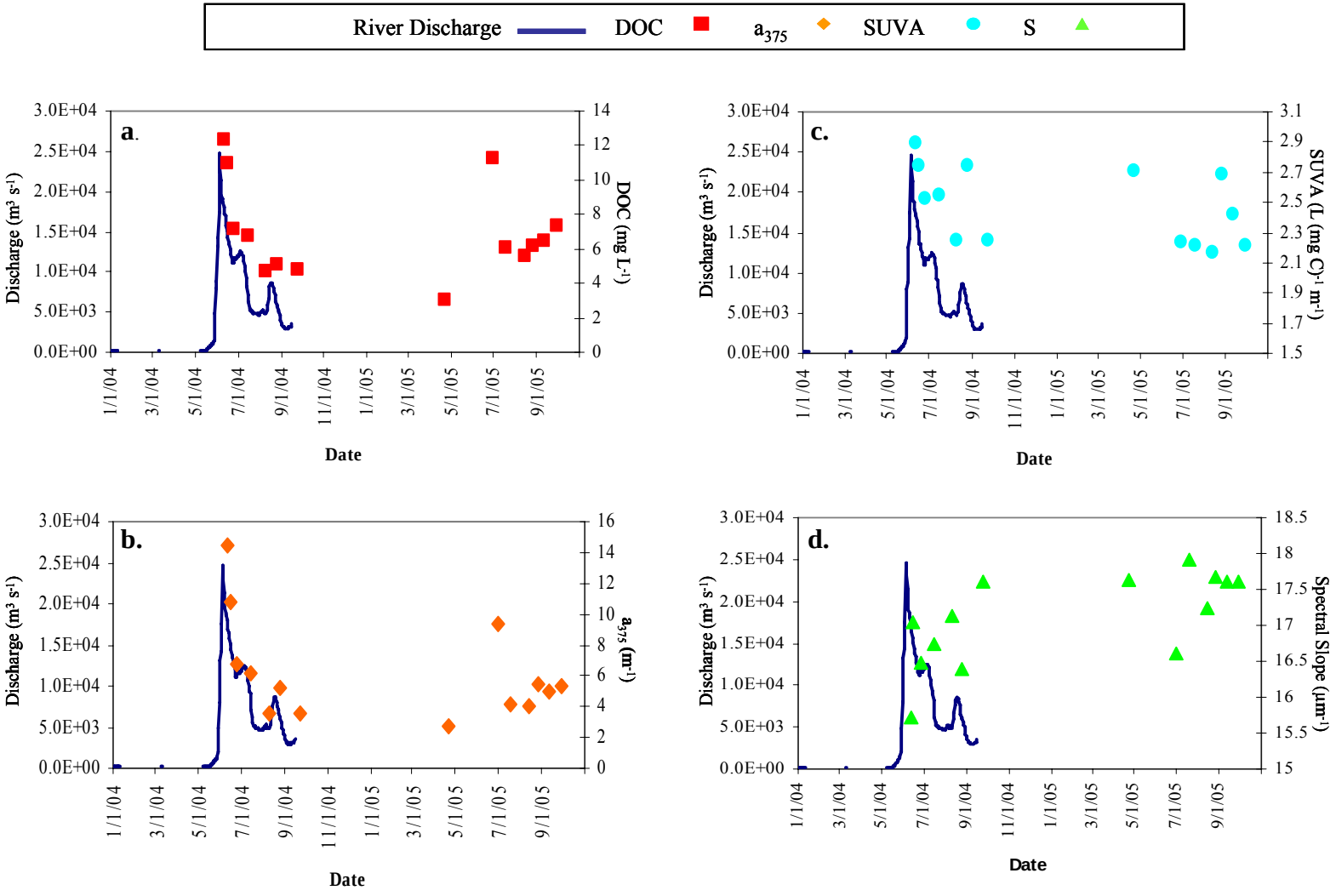

Figure 27. Kolyma River discharge ($m^3 s^{-1}$), and a) Dissolved organic carbon (DOC; mg L^{-1}), b) Absorption coefficient at 375 nm (a_{375}; m^{-1}), c) Specific ultraviolet absorption coefficient (SUVA; $L(mg\ OC)^{-1}m^{-1}$) and d) Spectral slope (S; μm^{-1}) for the years 2004 and 2005.

representative of peak flow (6/11/04, 6/30/05) (Figure 24bd). Minimum fluorescence was found in base flow samples (Figure 24ac). Locations of maximum fluorescence remained at Ex:240, EM:425-475 and Ex:315, Em:400-475 (Figures 30abcd) with intensity changes occurring seasonally. Maximum fluorescence in the Kolyma was similar to the Yukon and Ob, but much less than the Yenisei and Lena. Minimum fluorescence intensity in contrast, is similar to the Ob but greater than the Yukon.

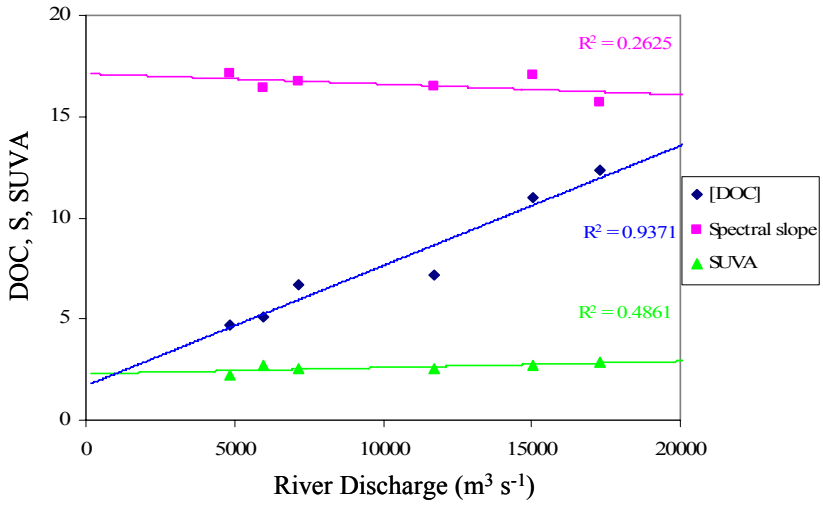

Figure 28. Relationship of Kolyma discharge to DOC (mg L^{-1}), spectral slope (μm^{-1}), and SUVA (L (mg OC)$^{-1}$ m^{-1}).

Lignin Phenols

LOP concentrations were highest on the first day of sampling in 2004 and decreased with the progression of the season. Σ8 decreased from 94.8 to 8.0 µg L^{-1} and Λ8 from 0.68 to 0.14 mg LOP (100mg OC)$^{-1}$ (Figure 31ab; Table 7). In 2005, Σ8 increased from 3.1 µg L^{-1} to 40.9 µg L^{-1} at peak flow and decreased in August and October (Figure 31a). Σ8 are similar to the Yukon, but significantly less then the

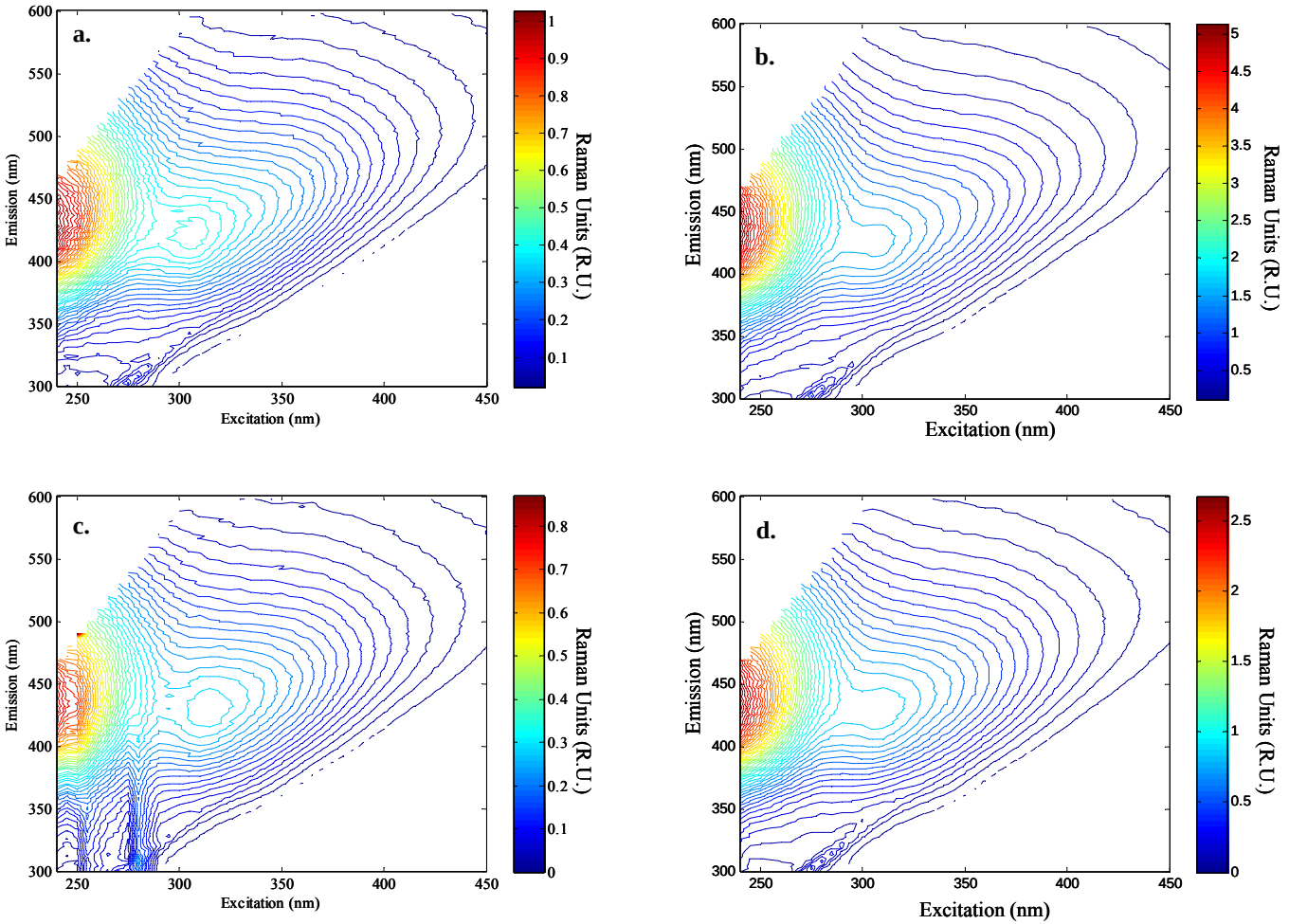

Figure 29. Fluorescence EEM's measured in Kolyma samples from low flow (a,c) and peak flow (b,d) conditions in 2004 (upper panals) and 2005 (lower panals). Note each subplot is on a different scale.

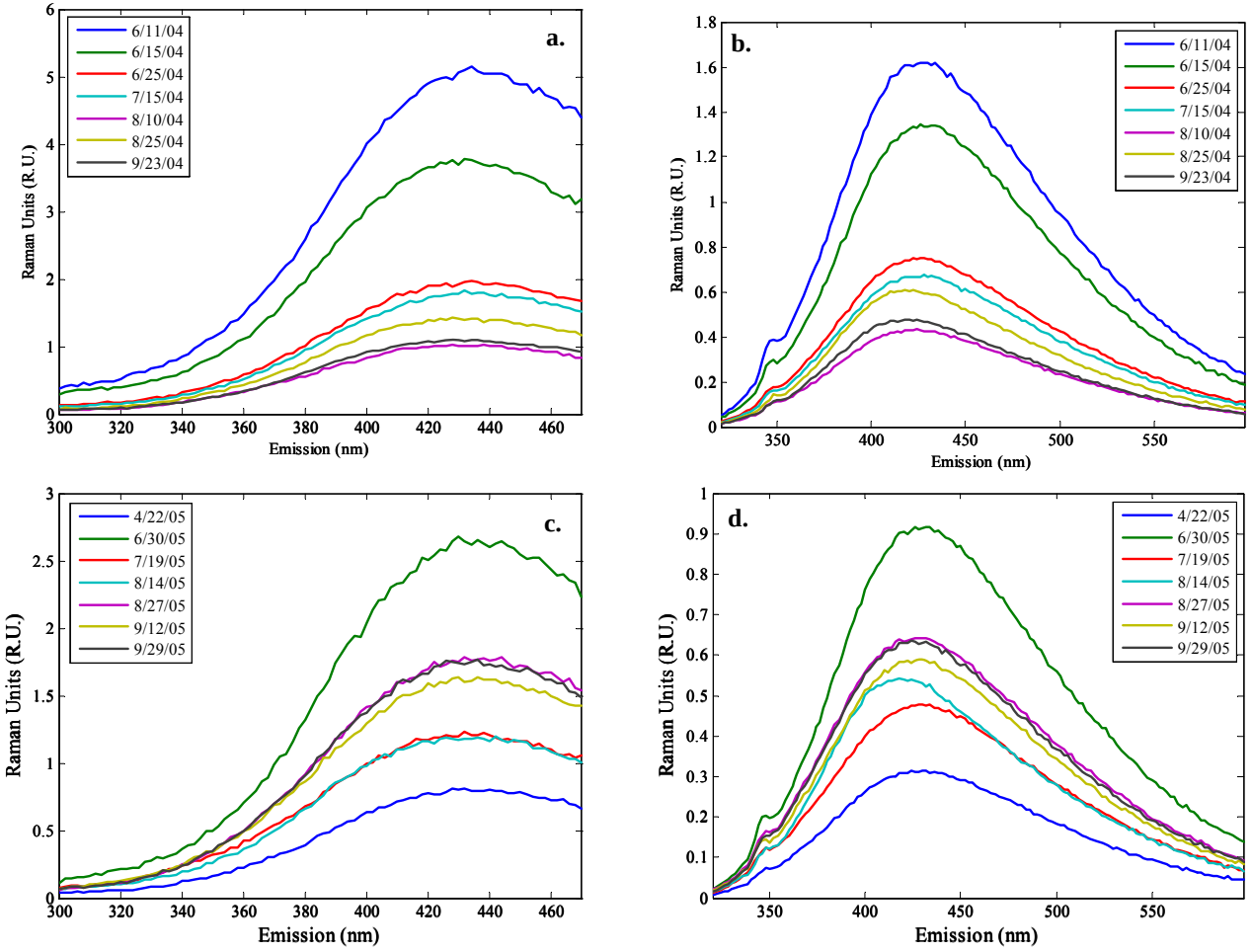

Figure 30. Seasonal variation in the maximum fluorescence intensity measured at excitation 240 nm (a & c) and 315 nm (b & d) for the Kolyma River in 2004 (a & b) and 2005 (c & d).

Yenisei and Lena. Λ8 similarly increased from 0.20 mg LOP (100mg OC)$^{-1}$in April to 0.34 mg LOP (100mg OC)$^{-1}$ in late June then returned to low levels for the rest of the season (0.06 mg LOP (100mg OC)$^{-1}$) (Figure 27b; Table 7). Carbon normalized yields were slightly smaller than the Yenisei and Lena but much higher than the Ob, Yukon, and Mackenzie. The highest (ad/al)v ratio (1.96) measured in this study was recorded mid-June sample. In 2004, (ad/al)v ratios decreased (1.19) similar to other rivers as the river returned to base flow in 2004 (Figure 31c). In 2005 (ad/al)v ratios increased from 0.81 at base flow to 1.54 at peak flow (Figure 31c). With the exception of the mid-June sample from 2004, (ad/al)v fell within the range of other rivers. S/V ratios seem to be highest at peak flow samples. In 2004 the highest value (0.58) was measured in the mid June sample; the rest of the year values fell within the range of 0.37-0.44 (Figure 31d). Similarly, in 2005 S/V values increased from ~0.25 to 0.53 then decreased again (Figure 31d). C/V ratios for both seasons were similar to the Lena and Yenisei varying between 0.05-0.14 (Figure 31d). The exceptions were the June samples from both years (0.23 and 0.18) which seemed enriched at peak flow (Figure 31d). In 2004, CAD/FAD ratios slightly increase from peak flow (0.44) to base flow (0.82) with a slight dip (0.64) in the June sample (Figure 31e). CAD/FAD ratios were more scattered in 2005 ranging from 0.41 to 0.91 (Figure 31e), but showed no trend. PON/P ratios were fairly constant in both 2004 and 2005 ranging from 0.12 to 0.26; with the only exception being the sample from late June (0.55; Figure 31e). DiBA/V and P/(V+S) ratios increase from peak flow (0.27, 0.23 respectively) to base flow (0.72, 0.60, respectively) in 2004 (Figure 31f). In 2005 the DiBA/V ratios are scattered between 0.47 and 0.83 whereas P/(V+S) drops from 1.15 at peak discharge to ~0.30 at base flow (Figure 31f). Again, the ratios of CAD/FAD, P/(V+S) and DiBA/V were generally lower for the Kolyma, Yenisei and Lena than the Mackenzie, Yukon, and Ob.

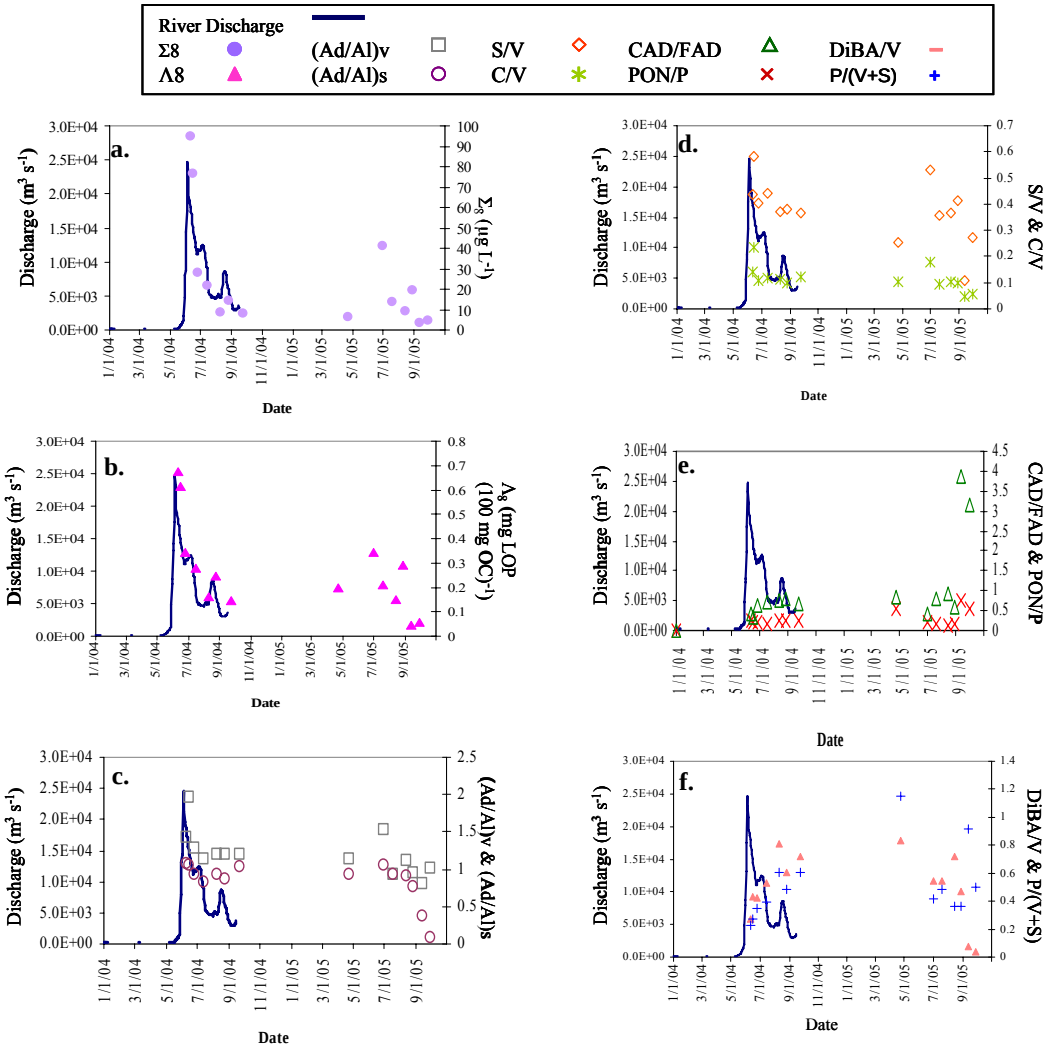

Figure 31. Kolyma River discharge and a) Sigma 8 (Σ_8; µg/L), b) Lambda 8 (Λ_8; mg LOP/ 100 mg OC), c) Acid to aldehyde ratios for vanillyls and syringyls, d) Syringyls/Vanillyls (S/V) & Cinnamyls/ vanillyls (C/V), e) p-coumaric acid/ferulic acid (CAD/FAD) & p-hydroxybenzaldehyde/total p-hydroxy group (PON/P), f) 3,5-dihydroxybenzoic acid/vanillyl (DiBA/V) & total p-hydroxy group/(vanillyl + syringyl) (P/(V+S))

CHAPTER V

DISCUSSION AND CONCLUSION

Dissolved Organic Carbon

River break-up was in late-May or early-June. Carbon concentrations were largest during this time, which agrees with other studies on Arctic rivers (Finlay et al. 2006; Guo and Macdonald 2006) (Figures 2a, 7a, 12a, 17a, 22a, and 27a). Soils are still frozen during break-up causing a flushing effect of soluble material off the surface of the watershed raising DOC concentrations in rivers. Previous studies (Carey 2003; Finlay et al. 2006; Guo and Macdonald 2006) have shown a hysteresis effect where DOC concentrations are highest on the ascending limb of the hydrograph in watersheds underlain with permafrost. Our samples were all taken at highest discharge or on the descending limb of the hydrograph so peak DOC discharge was likely missed. In July, August, and September the river returns to base flow conditions and the active layer of surface soils deepens (Hinzman et al. 1991). During this time period, DOC penetrates deeper into the soil and has a longer residence time within the soils where sorption and/or microbial processing lowers dissolved carbon concentrations (Cronan and Aiken 1985; Guggenberger and Zech 1994; Kaiser et al. 2004; Kaiser et al. 1996; Kawahigashi et al. 2006; Qualls and Haines 1992). In late summer-early fall DOC concentrations decreased by ~50-85% (with the exception being the Mackenzie River which in 2005 only dropped by 15%). This reduction suggests there may be a dilution effect but also losses due to sorption and microbial degradation. Optical properties and lignin suggest both mechanisms are contributing to lowered carbon values (see below). During the winter when the rivers were supported by groundwater, carbon concentrations were lowest. This water has had the longest possible flow path through the soils and DOC has

been further removed from the soil solution (Cronan and Aiken 1985; Guggenberger and Zech 1994; Kaiser et al. 2004; Kaiser et al. 1996; Kawahigashi et al. 2006; Qualls and Haines 1992).

Overall annual DOC exports (Table 6) agree with other studies (Rachold et al. 2004; Anderson 2002; Goni et al. 2000, Striegl et al 2007, Finlay et al. 2006). Generally DOC concentrations from the Mackenzie seem to have been overestimated by approximately 3 mg L^{-1}. Anderson (2002) refers to several studies where DOC concentrations range from 4.5-10.3 mg L^{-1}. The lower end of this range is very reasonable, but the largest DOC measured from the Mackenzie was 5.7 mg L^{-1} in this study. Similarly, another study (Hansell et al. 2004) estimated DOC in the Mackenzie at ~ 7 mg L^{-1}. Köhler et al (2003) calculated DOC export for the Yenisei (4.9 Tg yr^{-1}) and Ob (3.12 Tg^{-1}) which are generally in accordance with our values. Our estimates for the Lena are twice that of Lara et al. (1998) and Lobbes et al. (2000); however, this is probably the result of better seasonal sampling resolution capturing peak flow in this study. Cauwet and Sidorov (1996) show seasonal TOC flux to the Laptev sea from the Lena which is much lower than our estimates alone. Similarly, estimates made by Lobbes et al. (2000) for the Kolyma were approximately half of ours. Finlay et al (2006) reported DOC export from the Kolyma which were slightly higher than ours reflecting better sampling resolution surrounding peak flow, whereas our peak flow sample missed maximum discharge by six days in 2004. The same can be said for the 2004 estimates on the Yukon River, where Striegl et al. (2007) report slightly higher values than ours. Our estimates for the Mackenzie, Ob, Lena and Yenisei Rivers are likely also slightly underestimated because sampling missed peak DOC discharge.

Carbon flux estimates (Table 6) vary by river suggesting watersheds with either differing inputs or removal processes. It is difficult to argue that the inputs change substantially between rivers (with the exception of the Ob) because boreal forests are dominant across watersheds. It seems that river discharge (Figure 32a), river length (Figure 32b) and watershed area (Figure 32c) can explain between 57-84% of the variability in DOC export in these rivers. The lowest annual DOC export estimates were

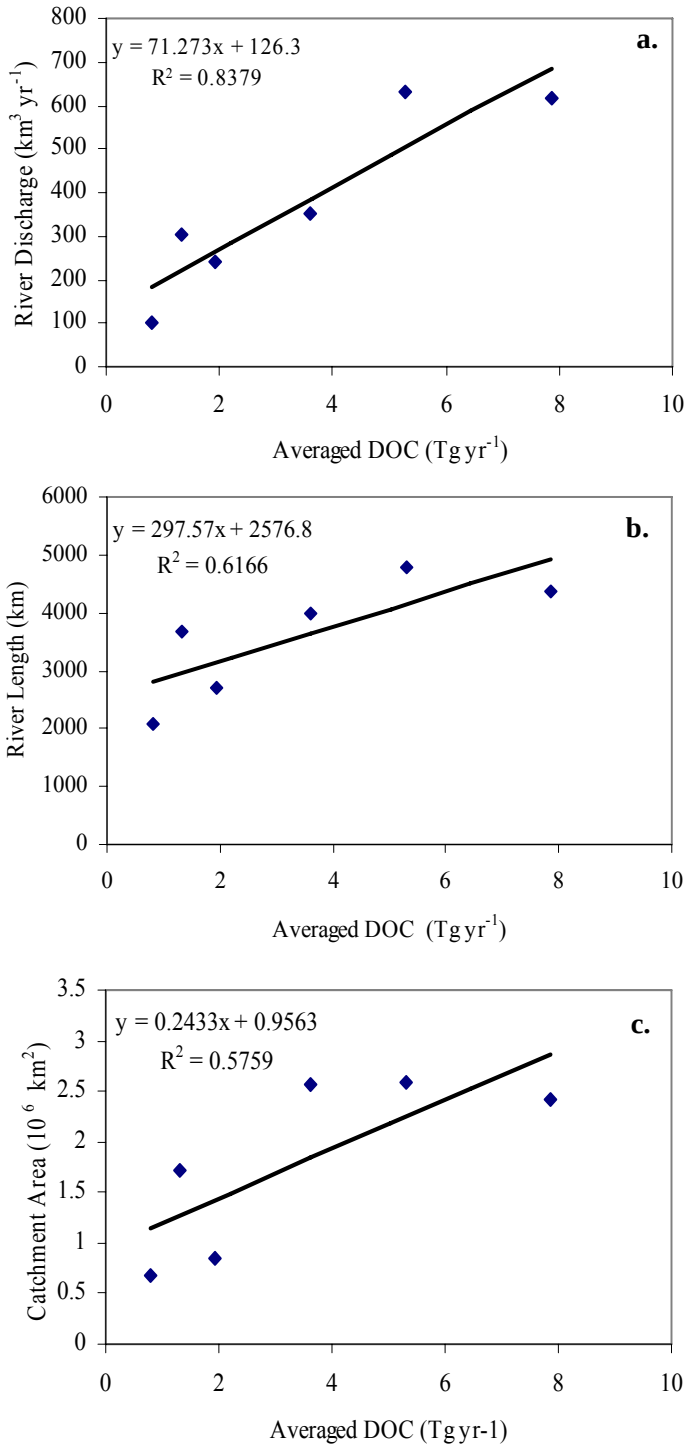

Figure 32. The average (2004 and 2005) DOC export (Tg yr^{-1}) for the Mackenzie, Yukon, Yenisei, Lena, Ob and Kolyma and a) river discharge (km^3 yr^{-1}), b) river length (km) and c) catchment area (10^6 km^2)

from the Mackenzie and Kolyma. The discharge weighted mean DOC concentrations were ~ two times larger in the Kolyma compared to the Mackenzie River, however, the annual export was only slightly larger. The Kolyma has the smallest watershed size and river discharge, but has the largest percentage of continuous permafrost of all the watersheds (Table 1). So, as the total carbon inputs may be smaller due to catchment size, a greater percentage of this material is making it into the river channel, especially at peak flow. Normalizing the annual export to watershed area (area weighted DOC export) shows that the Kolyma is exporting ~two times more dissolved carbon per area unit than the Mackenzie in 2004 (Table 6). Mackenzie River discharge is ~two and a half to three times that of the Kolyma and the catchment size is more than twice the area, but permafrost is restricted in the northern regions (Table 1). In the south the soils are commonly luvisols and podsols which have higher sorptive capacities (Guggenberger and Kaiser 2003). Therefore, it seems that in the southern region of the Mackenzie a smaller percentage of OM is making it into the river because it is retained in the soils via sorption and/or degradation (Qualls and Haines 1992; see below). Low area weighted DOC export estimates (Table 6) from the Mackenzie in general indicate that more carbon is being mobilized per square kilometer than the other rivers. The Lena has the largest annual DOC export, area weighted DOC export, and discharge weighted DOC concentrations than any other river (Table 6). This is likely the combination of large catchment size and distribution of permafrost (Table 1), as well as the influence of leptosol soils which are weakly developed shallow soils with less sorptive capacity (Kaiser et al. 2004). In 2004 the Lena has very similar annual exports as the Yenisei, however, the discharge weighted estimate is somewhat larger, which might be the result of dilution because the Yenisei had a larger river discharge. In 2005, however, the river discharge from the Lena was somewhat larger than the Yenisei but export was much higher, suggesting soil and permafrost distribution might be important processes limiting the carbon exports into the Yenisei. Soil types in the Yenisei watershed include podsols, podzoluvisols, inceptosols, leptosols, and cryosols (in order from greatest to smallest contribution) which have a greater sorptive capability (Stolbovoi et al. 1998). The Lena

in contrast, has a large distribution of podsols, with other dominating soil types being leptosols, inceptosols, and finally cryosols (Stolbovoi et al. 1998). Another important difference between watersheds is the amount of continuous permafrost underlying approximately 78-93% of the Lena's catchment whereas in the Yenisei it is only 36-55% (Zhang et al. 1999) suggesting that the distribution of permafrost has an important influence in increasing DOC transport into rivers. The Yenisei and Yukon are similar in discharge weighted mean DOC concentrations; however, the Yenisei's discharge and watershed area are about 3x larger than the Yukon so annual export of DOC is much larger in the Yenisei. The Yukon is also interesting because quantitative parameters like DOC and Σ8 (see below) drop rapidly after peak flow but the qualitative parameters (optical properties, Λ8, and LOP ratios) do not react nearly as quickly to hydrologic changes. This pattern may be the result of soil type distribution (cryosols and inceptisols dominant in Yukon); however, it also could be influenced by the mountainous terrain of Western Canada and Alaska creating the highest average slope (2.93 m km^{-1}) of the rivers studied here (Table 1). In 2005, it seems that more moisture (larger river discharge) was mobilizing more material into the Yukon River resulting in higher discharge weighted mean DOC concentration estimates, annual export as well as area weighted DOC export (Table 6). The Ob River has a very different type of discharge pattern and reflects the influence of the peat bog located within its watershed. The wetlands seem to not only act as a buffer which constrains DOC export until well after peak river flow but could also represent a significant source of carbon to the river. The annual export of carbon was approximately half of the Yenisei, but the discharge weighted DOC concentrations in the Ob was similar if not more than the Yenisei (Table 6). This was most likely dilution related because there is more DOC exported per unit area in the Yenisei than the Ob (Table 6). DOC concentration changes in the Ob are also not as dynamic between peak and base flow compared to other rivers.

Optical Properties

The absorption coefficient at 375 overall showed a strong relationship (r^2=0.88; n=84) with DOC indicating that this parameter could be used as a proxy for DOC concentrations in Arctic rivers (Figure 33). At higher DOC concentrations the relationship is weaker than at low DOC levels. The positive y-intercept indicates that about 1/3rd of the DOC pool is not absorbing at 375nm.

Optical properties during freshet support the flushing effect described above. High SUVA values at peak flow suggest material that is highly aromatic (Novak et al. 1992; Traina et al. 1990; Weishaar et al. 2003) (Figures 2c, 7c, 12c, 17c, 22c, and 27c). Striegl et al (2005; 2007) report similar though slightly larger SUVA values on the Yukon River for this time period. Striegl et al. (2005) further fractionated DOM using XAD resins and found that the hydrophobic material was most abundant. Neff et al. (2006) measured significantly higher SUVA's (~4.3 L mg C^{-1} m^{-1}) on the Kolyma at peak flow than on any samples in this study, but they also captured peak flow whereas our samples did not. Spectral slopes show DOM at peak flow has a larger molecular weight than at base flow (Stedmon et al. 2000). These values are in general agreement with others reported for the Yukon by Gueguen et al. (2006) who show a similar seasonal cycle in S. SUVA's and S's both indicate that at peak flow DOM is most likely derived from freshly leached vascular plant matter which has been washed off the surface of the

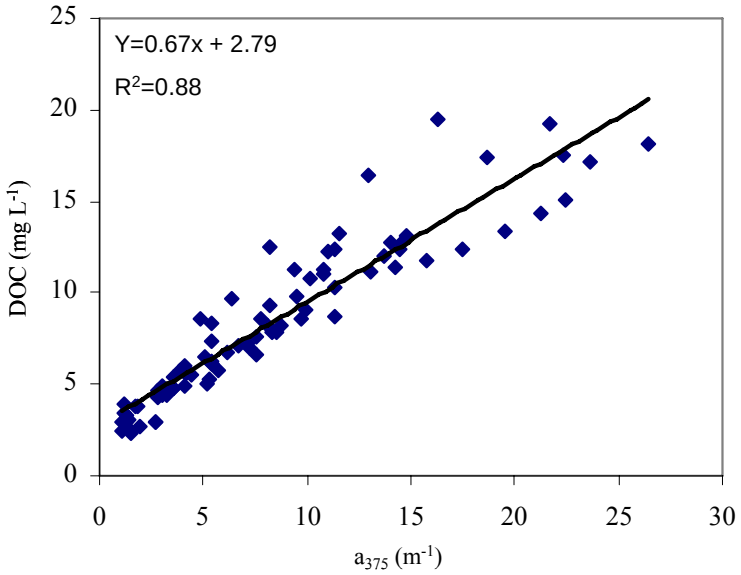

Figure 33. The relationship between Absorption coefficient at 375 nm and DOC data for all rivers, all seasons.

watershed into the river. In late summer-early fall SUVA values gradually decrease and spectral slopes gradually increase indicating the material is becoming smaller and less aromatic suggestive of minor degradation of OM in the soil during the warm months and or sorption of the highly aromatic fraction. Striegl et al. (2005, 2007) showed similar trends in reduction of SUVA in the summer-autumn, however, they also showed that the percent contribution of hydrophilic vs hydrophobic acids didn't change much between peak and base flow in the Yukon River. Neff et al. (2006) also showed reduced SUVA's on the Kolyma River, which were comparable to ours. The spectral slope measurements made by Gueguen et al. (2003) also increase during summer-autumn and agree well with measurements made in this study. SUVA's are generally equal to or lower in the winter compared to samples from the previous fall suggesting further degradation and/or sorption processes decreasing the aromaticity of OM. Spectral slopes are also equal to or higher in the winter compared to fall.

Comparisons between rivers don't show large differences in source material using optical properties. In the spring, SUVA's are generally ~15-30% larger from the Ob, Lena, and Yenisei (three largest rivers with largest discharge weighted DOC export) than for the Yukon, Mackenzie and Kolyma samples taken at the same time. Lowest values don't follow the same trend and are fairly similar across watersheds (1.4-2.2). Spectral slopes are not significantly different in the spring, however, the North American rivers values are somewhat larger than the Eurasian river values (especially Kolyma and Lena) during the winter. This is somewhat contradictory because spectral slopes show that during the winter material from the Yukon and Mackenzie is more degraded (less aromatic) than Eurasian rivers but SUVA's don't show any difference. There were not enough samples taken in order to do any statistical testing, but it could be that the differences shown are not larger than the statistical variation. Unlike DOC concentrations there was no lag period in the SUVA's and spectral slopes in the Ob River. The optical properties also didn't necessarily reflect DOC concentrations in the Yukon. In 2004 the gradual decrease and increase in SUVA's and S's, respectively was similar to other rivers showing that even though the amount of DOC dropped off rapidly with hydrologic state the sources of OM didn't change as much. The variability of SUVA's in autumn of 2005 was potentially due to light scattering by small particles in the sample. The Yukon samples often had small floating particles which complicate optical measurements. An effort was made to pre-filter (0.45 μm) all samples immediately prior to optical measurement, however, Yukon water samples were limited so this was not always possible. The DOC measurements in these samples agree well with the a_{375} measurement even though the water analyzed for DOC was not measured on the same day as optical properties. There was also evidence of this scattering in fluorescence (see below).

Fluorescence EEM's do not show any seasonal compositional differences between material at peak flow versus at base flow. The fluorescence maxima are associated with the humic peaks A and C that have been previously reported in the literature (Coble et al. 1990, Chen and Bada 1992, Coble 1996, McKnight et al. 2001,

and Chen et al. 2004) and are typically found in samples influenced by terrestrial organic material. Though the composition doesn't change the intensity of fluorescence increases several fold at peak flow, which generally can be assumed given the increasing carbon concentrations at this time. Fluorescence intensity decreases post-flood but shows the same maximums previously identified as humic peaks A and C. The fluorescence character suggests that seasonally, fluorescence properties don't change appreciably. This is partially because in boreal systems aquatic production of DOC seems to be low (Köhler et al. 2003, Zou et al. 2006) therefore the allothonous fraction being derived from vascular plants dominates the signal throughout the year (Gueguen et al. 2006). We are currently exploring alternative data analyses for the fluorescence scan data using parallel factor analysis.

Fluorescence intensity varies widely between rivers and seems to follow DOC concentrations. Maximum fluorescence was measured in the Lena which in 2004 was 2x larger than in the Yenisei. In fact fluorescence in 2005 for the Lena was half of what it was in 2004 even though carbon concentrations were similar. SUVA and lignin concentrations from the Lena were also substantially larger in 2004 than 2005. The Yukon, Kolyma, and Ob were of similar fluorescence intensity. The Yukon sample taken on 8/16/05 had an unidentified double peak at Excitation 275, Emission 320-340. The source of these peaks is unclear. There were lots of small particles in the Yukon samples prior to filtering but it doesn't rule out particles <0.45 μm contributing to this scatter. Fluorescence in the Ob follows the same trend as DOC concentrations, most likely because fluorescence measures a broader spectrum of organic moieties than SUVA and S's. The Mackenzie has very low fluorescence which corresponds to the low DOC concentrations in this river.

Lignin

Similar to DOC, LOP concentrations (Σ8) and carbon normalized yields (Λ8) were significantly larger at peak flow compared to base flow. As the river discharge decreased so did Σ8 and Λ8. The fact that Λ8 values decreased with decreasing

discharge indicates that lignin phenols contributed significantly less to the DOC pool during low and base flow conditions than during the peak flow. This suggests that there are shifts in the chemical composition of DOM, however, those changes are not as obvious from optical properties of colored DOM. This could be caused by the abundance of other chromophores not specifically measured in this study. Optical properties indicated that the peak flow DOM was of high molecular weight and rich in aromatic compounds. Concentration and export of lignin, similar to fluorescence was highest in the Lena and Yenisei and lowest in the Mackenzie. This again indicates that watershed characteristics such as size, discharge, permafrost extent, and soil type can have a large impact on the quantity of OC exported into the river. The only published lignin data for the Eurasian rivers was reported by Opsahl et al. (1999) and Lobbes et al. (2000). Lobbes et al. (2000) report Σ8 significantly lower than ours for the Yenisei, Lena, and Kolyma, however, they used a different methodology than we did which probably explains the inconsistencies. Opsahl et al. (1999) report Λ6 on UDOM (1kDa-0.2μm) for the Yenisei and Ob that are significantly larger than ours. The way Λ6 is calculated on UDOM makes it impossible to directly compare them to the numbers presented here.

Traditionally, the comparison of Λ8 and (ad/al)v has been used to show the diagenetic state of OM (Dalzell et al. 2005; Hedges et al. 1988a), with high (ad/al)v indicating advanced degradation. Figure 34a shows the relationship between Λ8 and (ad/al)v for the different hydrologic flow periods. It is clear that there is a separation of material in the different periods with peak flow having much higher Λ8 and (ad/al)v. In this study (ad/al)v are highest at peak flow in all rivers. If the traditional interpretation is used, then material at peak flow would be described as more degraded, which contrary to optical measurements. Other studies have interpreted high (ad/al)v as an indicator of enhanced leaching (Benner et al. 1990; Hedges and Weliky 1989), photo-bleaching (Opsahl and Benner 1998) or less sorption of DOM to the soil matrix (Duan et al. 2007). High Λ8 and (ad/al)v values in this study therefore suggest DOM at peak flow is derived from leaching of surface litter (Benner et al. 1990; Hedges and Weliky 1989). The

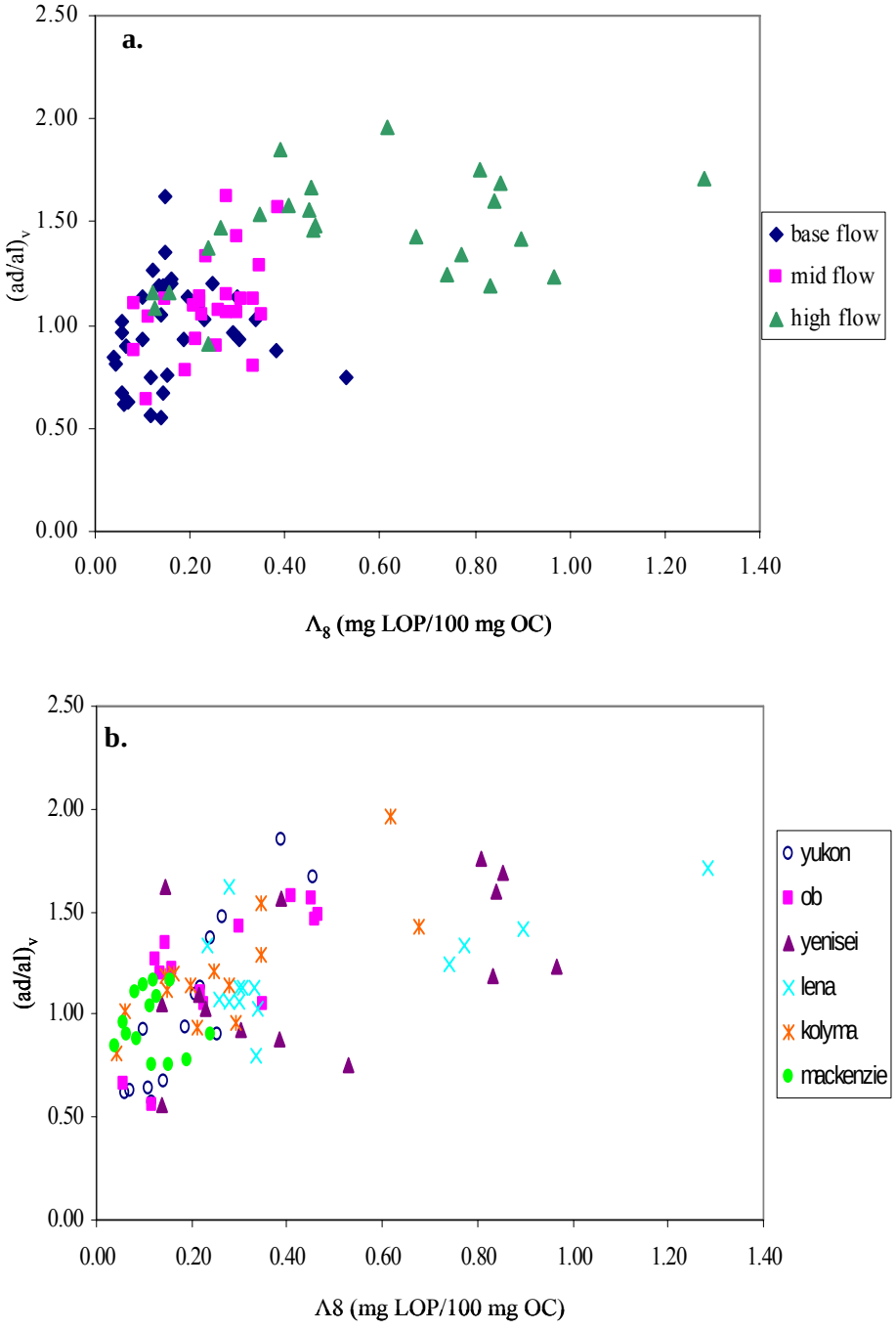

Figure 34. Relationship between lignin yield (Λ8) and ratio of vanillic acid/vanillin ((ad/al)v). a) all river data divided by hydrologic state, b) river to river comparison.

lignin precursor of vanillic acid is known to be bound by labile ester linkages (Hedges and Weliky 1989) allowing them to be more water soluble hence readily leached. Opsahl and Benner (1998) also showed that exposure of light during a 28 day incubation of Mississippi River water caused a 4 fold increase in (ad/al)v ratios. If photo-bleaching was contributing to high (ad/al)v at peak flow than these affects should be seen in optical properties and elevated S/V ratios (see below), however, there is no evidence of this. Duan et al. (2007) also showed an increased (ad/al)v value at higher flows (~1.5) compared to low flows (~0.8) for a black water river in Mississippi and suggested this was the effect of leached material having limited time in contact with mineral soils for sorption. These studies further support the leached and/or photo-bleached material present at peak flow is enriched with acidic side chains. (Ad/al)v drop steadily as the soils thaw and rivers return to base flow. This indicates a removal of the acidic fraction of lignin most likely through sorption. Several studies (Guggenberger and Zech 1994; Kaiser and Guggenberger 2003; Kaiser et al. 2004; Mcknight et al. 1992) have shown that acidic-DOM is readily sorbed to particles via ligand reactions (see below for a more detailed description of sorption). Winter time (ad/al)v ratios during lowest flow conditions are similar to autumn. The relationship between (ad/al)v and Λ8 is generally consistent across rivers (Figure 34b) with slightly elevated values from the Lena and Yenisei and lower values from Mackenzie. Lobbes et al. (2000) report slightly higher (ad/al)v for the Lena, substantially lower (ad/al)v for the Kolyma, and similar (ad/al)v ratios for the Yenisei. Opsahl et al. (1999) found slightly higher (ad/al)v in ultrafiltered-DOM than we did in C18 extracts.

S/V and C/V ratios are used to determine the contribution of angiosperm, gymnosperm, woody and non-woody tissue. Figure 35a shows the relationship between S/V and C/V ratios and suggests that hydrology does not contribute to source shifts of terrestrial DOM to the rivers. Figure 35b is a river to river comparison of the relationship between S/V and C/V ratios and includes shaded boxes indicating where different types of vegetation plot in relation to S/V and C/V (Hedges and Mann 1979). This relationship indicates DOM is a mixture of inputs mostly from gymnosperm

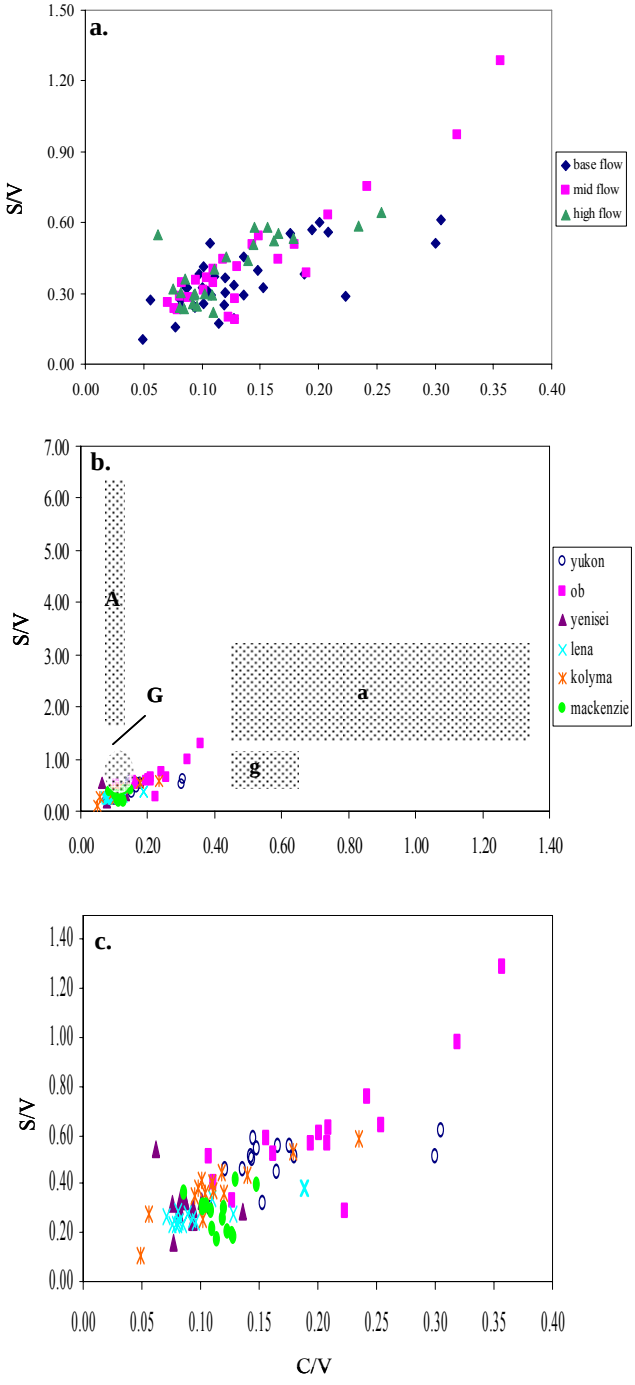

Figure 35. Comparison of cinnmyls/vanillyls (C/V) to syringyls/vanillyls (S/V). a) All river data divided by hydrologic state and b) river to river comparison. Highlighted regions show the composition of various plant material of according to Hedges and Mann (1979). (A)-woody angiosperms, (a)-non-woody angiosperms, (G)-woody gymnosperms and (g)-non-woody gymnosperms. C) expansion of x and y axis from subplot b.

vegetation with minor inputs by angiosperms. Lobbes et al. (2000) report significantly lower S/V ratios for the Yenisei and Lena but comparable S/V ratios for the Kolyma. Opsahl et al. (1999) report higher S/V on UDOM which might reflect the more degraded nature compared to DOM (<0.45μm). C/V ratios reported by Lobbes et al. (2000) were consistent with ours. Overall, inputs of DOM seem to be consistent across watersheds (Figure 35bc). The exception would be the Ob, which shows elevated S/V and C/V in its mid-flow state, when carbon concentrations as well as fluorescence intensities are maximum (Figure 36a). Mechanisms that would elevate S/V ratios would be the presence of angiosperm vegetation and photo-chemical degradation (Opsahl and Benner, 1998). As explained above and previously reported (Opsahl et al. 1999) photo-oxidation is most likely not important in these systems. Therefore source vegetation is probably the cause and indicates that there is enhanced carbon input from either the peat bog or the southern regions were angiosperm vegetation is more abundant. Spectral slopes and SUVA's both indicate this material is slightly more decomposed than at peak river flow, suggesting this material has had a longer residence time, potentially in the peat bog. River to river comparison of C/V ratios are also low suggesting the contribution of soft tissue is minimal in these watersheds (Figure 35c). As with S/V ratios there is very little seasonal change in C/V ratios in these rivers (Figure 35a), the exceptions were in the Ob (Figure 36a), Kolyma (Figure 36b), and potentially in the Yukon (not shown). As explained above for S/V during mid-flow the major source of OM in the Ob River is potentially the peat bog. Vegetation in these wetlands includes grasses that would elevate C/V. On the other hand, direct measurements on DOM from a bog lake near Murmansk, Russia had low S/V and low C/V values (Amon, unpublished data). In the Kolyma, C/V ratios at peak flow are ~40% larger than at base flow. The Kolyma River is dominated by larch forest that drop their needles at the end of the season. Elevated C/V might reflect leaching from these needles because cinnamyls tend to be loosely associated to lignin and non-lignin (carbohydrates, cutin) macromolecules by ester linkages (Houel et al. 2006; Opsahl and Benner 1993; Opsahl and Benner 1995). For the Yukon, it seems that p-coumaric acids are generally more abundant (high CAD/FAD;

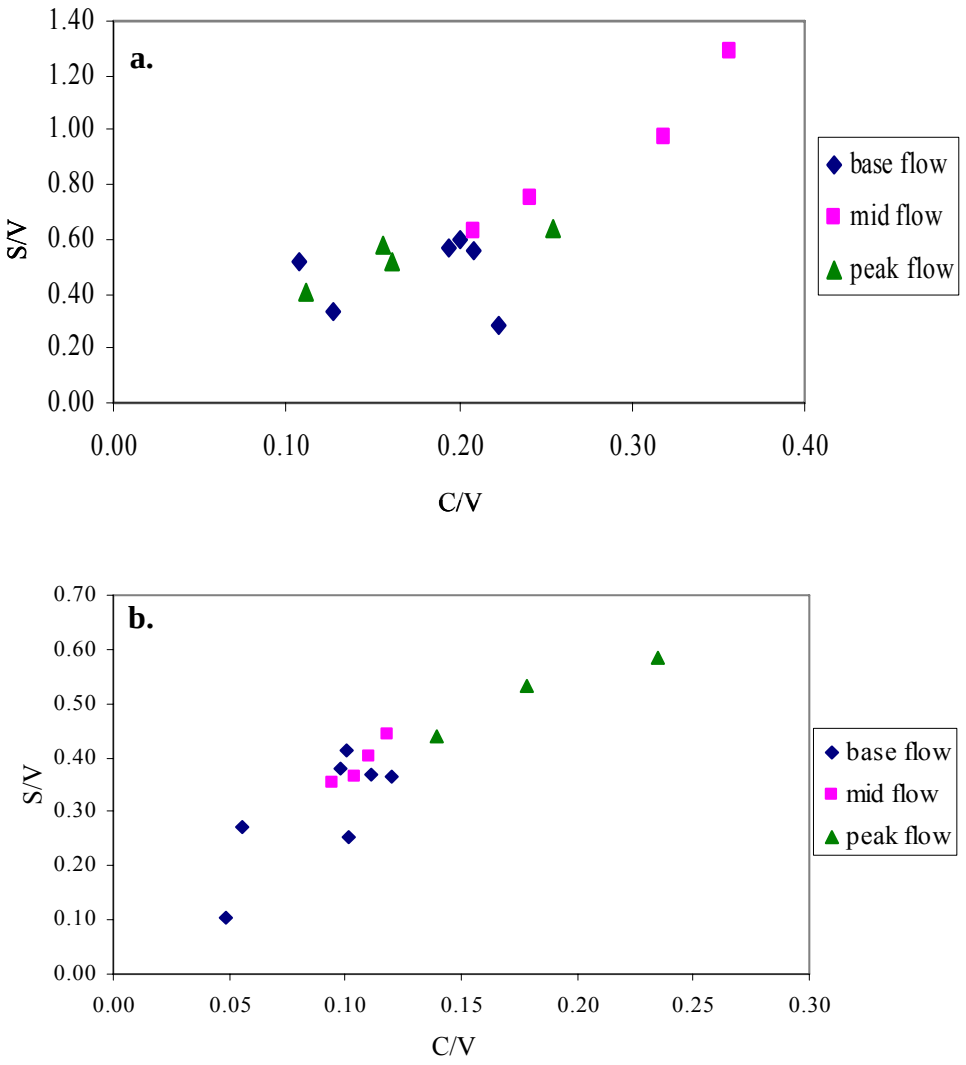

Figure 36. The relationship between C/V and S/V divided into different hydrological states for the a) Ob and b) Kolyma rivers.

see below) at base flow than at peak flow resulting in elevated C/V ratios. These samples need to be interpreted with caution because they were not only low in carbon but measured on the Varian GC/MS. Therefore in this case elevated C/V could be an artifact of either selective sorption by the C18 resins during the extraction and/or greater sensitivity of the Varian instrument to p-coumaric acids. However, it is plausible that more desorption (see below) of the cinnamyl groups from deep mineral layers is taking place at low flow as chemical conditions are changing due to extended periods of freezing conditions.

The ratio of p-coumaric to ferulic acids (CAD/FAD) can potentially be used as an indicator of degradation state, leaching, and sorption/desorption processes (Sanger et al. 1997, Houel et al. 2006). Dissolved FAD are known to be more susceptible to degradation relative to CAD, but CAD tend to be more soluble. These mechanisms ultimately lead to high ratios of CAD/FAD of LOP (Houel et al. 2006). In this study CAD/FAD ratios are lowest at peak flow generally increasing as the river returns to base flow and are highest during winter-time low flow (Figures 3e, 6e, 11e, 16e, 21e, 26e, and 31e). Optical properties and (ad/al)v suggest material at peak flow is not degraded but is freshly leached from surface litter therefore low CAD/FAD ratios seem to indicate degradation state in these systems. Increased ratios in the fall could be the result of degradation processes when soils are warmer. During the winter CAD/FAD ratios are high indicating further degradation as a result of a longer residence time within the soils (Houel et al. 2006; Sanger et al. 1997).

With a few exceptions, PON/P ratios were constant seasonally (Figures 3e, 6e, 11e, 16e, 21e, 26e and 31e). PON is known to have other non-lignin sources (algae) but the constant ratios indicate there was little in situ production of p-hydroxys in these rivers (Hedges et al. 1988b). Because we know that the p-hydroxys are essentially lignin derived we can interpret low peak flow P/(V+S) ratios as freshly leached (Figures 3f, 6f, 11f, 16f, 21f, 26f, and 31f). P/(V+S) is a specific biomarker for the brown-rot diagenetic pathway of lignin which leads to the demethylation of methoxylated V and S groups (Dittmar and Lara 2001). As the river returns to base flow P/(V+S) increase to their

highest values during winter. Elevated P/(V+S) support optical property measurements (and potentially CAD/FAD) indicating material is becoming less aromatic and smaller, or more degraded with increased residence time in the soils. The Eurasian rivers (Yenisei, Lena, and Kolyma) with more extensive permafrost in their watersheds have lower P/(V+S) ratios, with high values during the winter ranging from 0.47-1.16 and low values during freshet 0.15-0.23. Whereas the north American rivers and the Ob have much higher values both at low flow (0.69-3.95) and high flow (0.26-0.68). This suggests that fungal degradation of lignin is more extensive in soils with less permafrost.

Finally 3,5-dihydroxybenzoic acid also has non-lignin sources and is thought to be derived from tannins and other flavonoids in cells of degraded plant tissues or macroalgae (Houel et al. 2006; and references therein). There are no macroalgal sources of carbon in Arctic rivers therefore it can be assumed that as vascular plant tissue becomes more humified this ratio will increase. The ratio of 3,5-dihydroxybenzoic acid over total vanillyl (DiBA/V) is complementary to P/(V+S) and shows that DOM at peak flow is less humified relative to base flow (Figures 3f, 6f, 11f, 16f, 21f, 26f, and 31f). As the river returns to base flow values increase, reaching their highest values during winter. Similar to P/(V+S) the rivers with the most permafrost (Yenisei, Lena and Kolyma) have the smaller DiBA/V ratios suggesting that DOM is less humified.

Sorption

At high-flow conditions DOM was characterized as relatively more aromatic, with a larger molecular weight, and high concentrations of lignin phenols that were enriched in acidic constituents. During the peak flow season the soils in the watershed are still largely frozen and most of the moisture in the watershed is transported to the river channel by surface run-off rather than percolation. In July, August, and September the surface soils thaw and the active layer deepens causing a diversion of flow paths into the soils which is more favorable for DOM sorption (Hinzman et al. 1991). The main soils in these watersheds are podsols, inceptisols (cambisols), and podzoluvisols, with leptosols being abundant in Yenisei and Lena and histosols dominant in the Ob

watershed. Cryosols are also an important soil type in all watersheds. These types of soils are all involved in sorption to varying degrees. As the DOM passes through the soil layers there is a chromatographic separation of material where hydrophobic material is removed preferentially to the hydrophilic acids (Guggenberger et al. 1994; Kaiser et al. 1996; Kaiser and Zech 1999). The DOM we measured at peak flow is characteristic of largely hydrophobic material, whereas at base flow it might be described as slightly more hydrophilic (Guggenberger et al. 1994). Studies (Guggenberger et al. 2004; Kaiser et al. 2002, 2004) have shown that the hydrophilic material is depleted in lignin and enriched in microbial derived sugars, amino sugars and nitrogen. Kawahigashi et al. (2006) found that cryosols had a greater sorptive capacity than inceptisols in the Yenisei drainage basin. Their findings indicated that cryosols with a thick organic layer only release a small amount of DOM into the mineral soils which is rich in hydrophobic acids but release a large amount of hydrophilic material into the river. Another study (Kawahigashi et al. 2004) found that 60% of Yenisei DOM is hydrophobic. This observation was explained by rapid lateral flow paths through the organic layer of this soil type. In inceptisols, which is an abundant soil type in the south of their Yenisei study area, less OM was adsorbed with a greater proportion of hydrophilic constituents discharged into the river (Kawahigashi et al. 2006). This is because in soils with less sorptive capacity the hydrophobic components will compete with and often displace their hydrophilic counterparts for reactive sites. Also, because these southern soils are warmer and better drained there is more microbial decomposition of OM releasing hydrophilic DOM. Also, during the winter groundwater will mobilize hydrophilic material into the rivers (Kaiser et al. 2002). This is supported by optical properties and lignin parameters which show that DOM is more degraded (smaller and less aromatic, elevated CAD/FAD, P/(V+S) and DiBA/V ratios) and has smaller lignin concentrations and lower (ad/al)v ratios. This mobilization might involve desorption, however, these mechanisms are not as well understood. One possibility leading to desorption is space limitation. As loading increases on particles and space limits how many interactions each molecule can have, there could be desorption as physical or chemical conditions

change within the soils (Guggenberger and Kaiser 2003). The hydrophilic fraction will generally be desorbed preferentially because its more soluble and hydrophobic interactions are stronger (Kaiser and Zech 1999). Studies (Guggenberger and Kaiser 2003; Kaiser and Zech 1999) have shown that at low loading, hydrophobic material can be involved in several ligand interactions making them very stable and difficult to remove. As stated above, desorption can occur as chemical conditions change such as increased SO_4^{-2}, and $H_2PO_4^-$ concentrations or increased pH (Kaiser and Zech 1999). Preliminary data (http://ecosystems.mbl.edu/partners/default.htm) suggests there is a slight drop in pH during the wintertime, but probably not enough to affect sorption/desorption processes. However, SO_4^{-2} concentrations increased ~25-75% (http://ecosystems.mbl.edu/partners/default.htm) during the winter for the Lena, Ob, and Mackenzie which might be enough to compete for binding sites with OM.

Conclusion

This study showed that ultimately the sources of DOM are seasonally consistent in these large rivers. Absorbance parameters suggest material is slightly more aromatic and has a larger molecular weight at peak flow relative to base flow conditions. Fluorescence EEM's showed that DOM is essentially dominated by humic material (peaks A and C) regardless of sampling time. Lignin ratios indicated that material at peak flow is derived from surface litter leachates whereas at base flow hydrophobic DOM is removed by preferential sorption from the soil solution. Lignin ratios also generally agree with absorbance parameters showing that DOM becomes slightly more

decomposed during base flow conditions. In contrast to the quality of DOM which changes only slightly, the quantity changes dramatically. At peak flow DOC concentrations and fluorescence increase many fold reflecting surface run-off. During this time soils are frozen so transfer of DOM from soils to the river channel is dominated by surface run-off. As soils thaw, flow paths are diverted and sorption and/or degradation processes remove DOC thereby reducing the amount of carbon reaching the river channel.

It seems that the main mechanism governing the abundance and chemical composition of DOM in Arctic rivers is the relative contribution of surface run-off versus soil infiltration. Watershed characteristics determine the relative importance of the two and in consequence DOM composition and concentration in these large river systems. Large watersheds like in this study are very heterogeneous with respect to climate, vegetation, geology, permafrost, soil types, diagenesis, etc. and are difficult to differentiate from each other in terms of DOM concentration and composition. DOM quantity and quality represents an integrated signal that reflects the complex interplay of all these factors.

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